

# THE DYEING OF COTTON FABRICS

BY FRANKLIN BEECH: THIRD EDITION, REVISED AND ENLARGED BY

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## CHAPTER I.

### STRUCTURE OF THE COTTON FIBRE.

**Dyeing of Cotton.**—No subject is more important to the bleacher, textile colourist, or textile manufacturer than the structure and chemistry of the cotton fibre which each of these individuals treats, in his own special way, to attain the object which he has in view. By the term *Chemistry* we mean not only the composition of the pure fibre itself, but also that of the impurities with which it is contaminated. The fibre must be freed from these impurities so as to be in a fit and proper condition to receive, and permanently fix, the special individual dye or mixture of different dyes and the adjuncts required to aid in fixing the dye on the fabrics. This preliminary cleansing applies more especially to colours of a delicate tint which the natural colour of the impurities would soil and degrade. In the fibres it would be absolutely impossible to dye cotton of a dirty natural yellow (whitey brown) colour a delicate shade of pure blue. The result would in fact be a dirty pea green. To get a pure blue tone the cotton must be absolutely white. The chemistry of cotton, to be brief, includes, therefore, the reactions which the crude fibre and its impurities undergo under the action of acids, alkalis and salts. The action of acids, alkalis and salts on purified cotton fibre itself falls within the domain of its chemistry. Pure cotton fibre consists of pure cellulose, and the chemistry of cellulose is a wide subject. As a matter of fact, the chemistry of two classes of compounds of cellulose, its acetates and its nitrates, each occupies individually a very

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wide field, but a field which it is only necessary for us to glance at in passing. The chemical changes which pure cotton fibre and its impurities respectively undergo under the action of chemical reagents have a very important influence on the operation of bleaching and dyeing cotton fabrics and on the strength and durability of the fabrics after being so treated. Bleaching operations, for instance, must be performed with extreme delicacy and care. Otherwise the fabric will run great risk of being tendered. Textile fibres occur in or on plants in three forms : (1) as cuticle or ciliary hairs, of no practical use, being much too short for preparation of textile fabrics ; they play an important part in the physiology of the plant ; (2) as seed hairs (fibres attached to the seeds of many plants, e.g. the common thistle and dandelion) ; the cotton fibre from species of bombax belongs to this group of seed hairs, while there are others, kapok from *eriodendron anfractuosum*, the white silk cotton tree,<sup>1</sup> etc., that

<sup>1</sup> According to Watt (*Commercial Products of India*), p. 522, Gamble, quoting Irepjen, very properly remarks that the kapok cotton is obtained not from the testa of the seed but the wall of the capsule. This, continues Watt, is perhaps more than a botanical peculiarity, and accounts doubtless for some of the characteristics of the floss which is used in nature as a packing material for the seeds, but is not, like cotton, formed from the seeds themselves. Kapok is of better quality than the corresponding cotton of bombax as it is more elastic and less liable to knot. Watt further states that the increasing demand for this floss in Europe, according to some writers, necessitates the belief that it is being used for textile purposes. But it is too fine, light, smooth and slippery, and, according to Merill, brittle to be easily spun unless used as an admixture with other flosses. Owing to its non-hygroscopic quality, its lightness and its resiliency, it is largely worked up for cushions, pillows, chairs, bedding. Life-jackets may be padded with it and coated with waterproof and airproof cloth. The U.S. Navy prescribes kapok for use on motor boats. The increased demand is due to its extended use as a resilient packing material for buoys.—Sir George Watt, *Commercial Products of India*, pp. 521-5.

Merill, Botanist of the Bureau of Science, Manila, describes the testa thus : An oblong 5-celled, 5-valved capsule about 15 centimeters long and 5 centimetres thick, the valves glabrous outside, inside silky, the seeds globose, black, numerous, completely surrounded by abundant white or somewhat brownish long shining silky hairs, the kapok of commerce.

have been tried from time to time in spinning and weaving, but without much success. Seed hairs vary much in length, from  $\frac{1}{2}$  inch to  $1\frac{1}{2}$  inches or even 2 inches ; each fibre consists of a single unit. Whether it is serviceable as a textile fibre depends upon its structure, which differs in different plants, and also upon the quantity available and the nature of the impurities present.

(3) The fibres of the third class are by far the most numerous. They consist of the fibres lying between the bark or outer cuticle and the true woody tissues of the plant. This portion is known as the bast, and hence these fibres are known as "bast fibres." They are noticeable on account of the great length of the fibres, in some cases upwards of 6 feet ; but these long fibres are not single fibres, but are really bundles of the ultimate fibres aggregated together to form one long fibre. Thus the ultimate fibres of jute are really very short—from  $\frac{1}{10}$  to  $\frac{1}{8}$  of an inch in length ; those of flax are somewhat longer. Jute, flax, China grass and hemp are common fibres derived from the bast of the plants. There is an important difference in the degree of purity between seed fibres and bast fibres. While seed fibres are fairly free from impurities—cotton rarely containing more than 5 per cent.—bast fibres contain a large proportion of impurity, from 25 to 30 per cent. as they are first obtained from the plant, and this large quantity has much influence on the extent and character of the treatments to which they are subjected.

Seed hairs are cylindrical and tubular and have thin walls, bast fibres are more or less polygonal in form and are not essentially tubular, having thick walls and small central canals.

**The Cotton Fibre.**—The seed hairs of the cotton plant are separated from the seeds by "ginning" and they then pass into commerce as raw cotton. In this condition the fibre is

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found to consist of the actual fibrous substance itself, containing, however, about 8 per cent. of hygroscopic or natural moisture, and 5 per cent. of impurities of various kinds ; the proportion and nature of cotton fabrics vary in different descriptions of cotton. As cotton fabrics pass through the operations of bleaching, as a preliminary to dyeing or printing, the impurities are eliminated.

**Impurities of the Cotton Fibre.**—Dr. E. Schunck many years ago investigated the natural impurities in cotton fabrics and found them to consist of the following substances :—

1. **Cotton Wax.**—This bears a close resemblance to carnauba wax, ceryl cerotate. It is lighter than water, has a waxy lustre, is somewhat translucent, is easily powdered, and melts below the boiling-point of water. It is insoluble in water, but dissolves in alcohol and in ether. When boiled with weak caustic soda it melts but is not dissolved by the alkali ; it can, however, be dissolved by boiling with alcoholic caustic potash. It appears likely that this wax is fairly uniformly distributed over the surface of the cotton fibre, and it is due to this fact that raw cotton is wetted by water only with difficulty.

2. **Fatty Acids.**—A solid, fatty acid, melting at 55° C. By analysis, this was shown to have the formula  $C_{34}H_{34}O_4$  (similar to that of margaric acid), but it was suspected to be a mixture of stearic and palmitic acids.

3. **Colouring Matter.**—Two brown colouring matters, both containing nitrogen, are present in raw cotton, one readily soluble in alcohol, the other only sparingly so. The brown colour of Egyptian and some other dark-coloured varieties of cotton is due to the presence of abnormal amounts of these brown colouring principles.

4. **Pectic Acid.**—This is the chief impurity in raw cotton, where it occurs as an amorphous gumlike substance of a light yellow colour. It is soluble in boiling water, and the solution

has a faint acid reaction. Acids and many metallic salts, e.g. mercury chloride and lead acetate, precipitate pectic acid from its solutions. Alkalies combine with it; pectic compounds form brown substances, and are but sparingly soluble in water; many of them can be precipitated by addition of neutral salts, like sodium and ammonium chlorides.

**Albumens.**—A small quantity of albuminous matter is found among the impurities of cotton.

Since the investigations of Schunck, however, it has been shown that the fatty matters present in raw cotton are very complex. Also, the chemical and mechanical treatment to which cotton is subjected, very considerably affects the amount of fatty matter which can be extracted from it by means of organic solvents. For instance, Knecht and Streat have found that American raw cotton, after complete extraction with benzene (0·63 per cent. of fat was thereby extracted) then yielded, after treatment with hydrochloric acid of 2° Tw. for fifteen minutes at 30°-40° C., 0·21 per. cent. of fat when again extracted with benzene.

The complex nature of the fatty matters present in raw cotton is evident from the work of Fargher and Probert, who examined the benzene extract obtained on the large scale from American cotton in silver form. They found the extract to contain gossypyl alcohol,  $C_{30}H_{62}O$ , carnaubyl alcohol,  $C_{24}H_{50}O$ , montanyl alcohol,  $C_{26}H_{54}O$ , phytosterols, palmitic, stearic and oleic acids, together with two complex hydrocarbons.

**Structure of the Cotton Fibre.**—The cotton fibre varies in length from 1 to 2 inches, not only in fibres of the same class but also in fibres from different localities—Indian fibres varying from 0·8 in the shortest to 1·4 in the longest stapled varieties; Egyptian cotton fibres range from 1·1 to 1·6 inches long; American cotton ranges from 0·8 in the shortest to 2 inches in the longest fibres. The diameter is about  $\frac{1}{250}$  of

an inch. When seen under the microscope fully ripe cotton presents the appearance of irregularly twisted ribbons, with thick rounded edges. The thickest part is the root end, or point of attachment to the seed. The free end terminates in a point. The diameter is fairly uniform through  $\frac{3}{4}$  to  $\frac{7}{8}$  of its length, the rest is taper. In Fig. 1 are given some illustrations of the cotton fibre, showing this twisted and ribbon-like structure, while in Fig. 1A are given some transverse sections of the fibre. Perfectly developed, well-formed cotton fibres always present the appearance of a collapsed

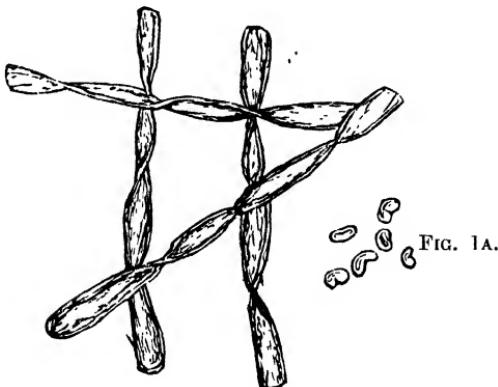


FIG. 1.—Cotton fibre.

cylinder, the walls being of considerable thickness when compared with the internal bore or canal.

But all varieties of commercial cotton contain imperfectly developed or unripe fibres, to a greater or less extent. These "dead fibres" neither spin nor dye well. Under the microscope these fibres differ in appearance from ripe fibres, since they are flatter, and the central canal is almost obliterated and the fibres are but little twisted. Dead fibres are thin, brittle, and weak. Contrast the structure of cotton with the fibre of kapok which consists of a single cell possessing a cylindrical shape, being rather thick at the base and

tapering gradually to the point. The base of the fibre is frequently swollen and exhibits a lace-like structure. The cell wall is usually very thin, occupying not more than one-tenth of the weight of the fibre. The cross section is circular and not flat as in the case of cotton. The inner canal is partly filled with a dried protoplasmic membrane. We have said kapok can only be spun with great difficulty, but from its bark a kind of string is spun, a fact which brings another class of fibres under view—the bark fibres.

**Composition of the Cotton Fibres.**—Of all the vegetable textile fabrics, cotton has the simplest chemical composition and is the type of all such fibres, the others differing from it in certain details. When stripped of the comparatively small quantities of impurities, cotton is found to consist of a substance to which the name of cellulose has been given. Cellulose is a compound of the three elements, carbon, hydrogen, and oxygen, C = 44.2, H = 6.3, O = 49.5 per cent., corresponding to the empirical formula  $C_6H_{10}O_5$ , which shows it to belong to the group of carbohydrates, the hydrogen and oxygen of which are present in the proportion necessary to form water ( $H_2O$ ).

Cellulose may be obtained in a pure condition from cotton by treatment with alkalis, followed by washing, then by treatment with hypochlorites, acids, washing and finally, drying. As thus obtained it is a white substance having the form of the fibre from which it is derived, showing a slight lustre, and is slightly translucent. Its specific gravity is 1.5, being heavier than water. It is characterised by being very inert, a property of considerable value from a technical point of view, as enabling the fibres to stand the various operations of bleaching, dyeing, printing, finishing, etc. Nevertheless, by suitable means, cellulose can be made to undergo various chemical decompositions which will be noted in some detail. Cellulose exposed to the air absorbs

moisture, this moisture being known as hygroscopic moisture, or "water of condition." The moisture content of cotton is about 8 per cent., and has a very important bearing on its spinning properties. Moisture makes the fibre soft and elastic, while absolutely dry cotton fibre is stiff, brittle, and non-elastic; hence it is easier to spin and weave cotton in moist climates or moist weather than in dry climates or dry weather. Cotton cellulose is insoluble in all ordinary solvents, such as water, ether, alcohol, chloroform, benzene, etc., and these agents have no influence in any way on the material, but it is soluble in some special solvents to be noted later on.

*Action of Alkalies on Cotton.*—The action of alkalies on cellulose or cotton is one of great importance in view of the universal use of alkaline liquors containing soda or caustic soda in the scouring, bleaching and dyeing of cotton, while great interest attaches to the use of caustic soda in the "mercerising" of cotton.

*Action of Dilute Alkali on Cellulose.*—Dilute solutions of the caustic alkalis, caustic soda or caustic potash, of from 2 to 7 per cent. strength, have but little action on cellulose or cotton, in the cold, even when a prolonged digestion of the fibre with the alkaline solution takes place. Caustic alkali solutions of from 1 to 2 per cent. strength have little or no action even when used at high temperatures and under considerable pressure—a fact of very great importance from a bleacher's point of view, as it enables him to subject cotton to a boil in kairs, with such alkaline solutions at high pressures, for the purpose of scouring the cotton, without damaging the fibre itself.

*Action of Concentrated Alkali on Cellulose—Mercerisation.*—Solutions of caustic soda of greater strength than 3 per cent. tend, when boiled under pressure, to convert the cellulose into soluble bodies, and as much as 20 per cent. of the

fibre may become dissolved under such treatment. The action of strong, cold solutions of caustic soda or caustic potash upon cellulose or cotton, however, is somewhat different.

In 1854, John Mercer found that strong cold solutions of caustic soda had a considerable effect on the fibre, causing it to swell and become gelatinous and transparent in its structure, each individual cotton fibre losing its ribbon-like appearance and assuming a rod-like form, the central canal being more or less obliterated. This is shown in Figs. 2 and 2A, where the fibre is shown as a rod and the cross-section

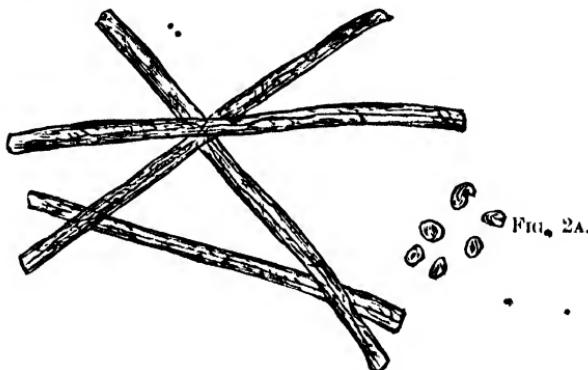


FIG. 2.—Mercerised cotton fibre.

in Fig. 2A has no central canal. This swelling is always accompanied by a longitudinal contraction.

At one time, it was thought that the caustic soda entered into chemical combination with the cotton to form such a compound as  $C_6H_{10}O_5 \cdot 2NaOH$ , but in recent years this has been questioned and to-day much doubt exists about the existence of such a compound. In any case, such a compound is extremely unstable, for all the caustic soda absorbed by cotton during its treatment with alkali can be completely removed by washing.

The treatment of cotton with alkalis, whereby swelling and

shrinkage occur, is known as mercerisation. Mercer pointed out the fact, now generally known, that after mercerisation cotton has an increased affinity for dyestuffs. More recently Knecht has shown this increased affinity to be proportional to the degree of mercerisation.

One point overlooked by Mercer, but subsequently discovered by Lowe, was that if during mercerisation or in the subsequent washing in water, the cotton was stretched to its original length, its lustre was thereby increased. This

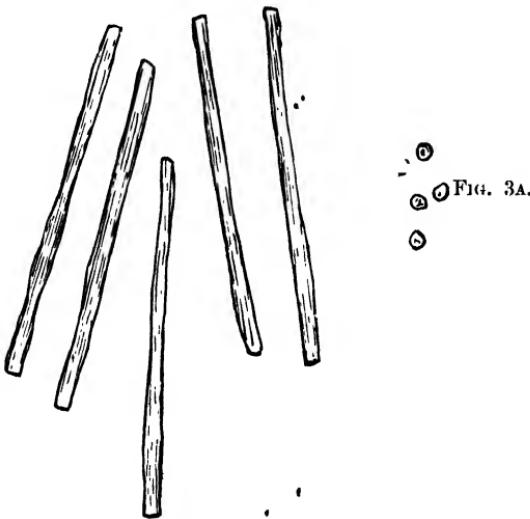


FIG. 3.—Mercerised cotton fibre.

was an important discovery, for to-day, mercerisation is almost solely carried out for the purpose of producing increased lustre. In general practice, the cotton yarn or fabric is padded with caustic soda of 45°-55° Tw., is then washed under tension, afterwards soured and finally thoroughly washed free from acid.

The structure of mercerised cotton fibre is shown in Figs. 3 and 3A.

*Action of Acids on Cellulose.*—The action of acids on

cellulose is a very varied one, being dependent upon several factors, such as the particular acid used, the strength of the acid, duration of action, temperature, etc. As a rule, organic acids—for example, acetic, oxalic, citric, tartaric—have no action on cellulose or cotton. Solutions of sulphuric acid or hydrochloric acid of 2 per cent. strength have practically no action in the cold, and if after immersion the cotton or cellulose be well washed there is no material change. This is important, as in certain operations of bleaching cotton and other vegetable fibres it is necessary to sour them, and this could not be done if dilute acids were harmful. When acid solutions are used at the boil, they have a disintegrating effect on the cellulose; the latter being converted into hydrocellulose, dextrines and sugar substances such as glucose. When dried after this acid treatment, the cellulose becomes brittle and readily falls to a powder. Under similar but less drastic treatment, cotton yarn would be weakened, that is, *tendered*. Generally the harmful action of an acid is proportional to its concentration and temperature.

*Action of Sulphuric Acid on Cotton.*—When cotton is immersed in concentrated sulphuric acid, it becomes gelatinous and finally dissolves, a sulphuric acid ester of the cellulose being formed. With prolonged treatment, sugar substances are produced. On dilution of the acid solution, cellulose is precipitated. These facts are utilised in the production of parchment paper, where ordinary paper is immersed for a few seconds in cold strong sulphuric acid and then immediately washed in water whereby it acquires a smooth, parchment-like surface.

*Action of Hydrochloric Acid—Hydrocellulose—Carbonising.*—Dilute hydrochloric acid of from 1°-2° Tw., used in the cold, has but little action on cellulose. Cotton immersed in acids of the strength named and then well washed

in water is not materially affected in any way. Boiling dilute acid, however, of  $10^{\circ}$  Tw. disintegrates cellulose very rapidly, the product being a white friable powder, which, when viewed under the microscope, appears to be fragments of the fibre used to prepare it. By further digestion with acid, hydrocellulose (the powdered product) is further converted into dextrin and sugar substances. Hydrocellulose is much more reactive towards chemical reagents than normal cellulose.

The formation of hydrocellulose has an important application in woollen manufacture. It is practically impossible to obtain wool free from vegetable fibres, and it is, therefore, often desirable to separate these vegetable fibres. For this purpose, the goods are passed into a bath containing dilute hydrochloric or sulphuric acid and are then dried. The acid thereby converts the cotton or vegetable fibres into hydrocellulose which, being friable, can be easily removed by washing, while the wool, not having been acted on by the acid, remains quite intact. The process is known as "carbonising." It may not only be done by means of the acids named but also by the use of acid salts, such as aluminium chloride, which, on being heated, are decomposed into free acid and basic oxide. For the same reason it is important to avoid the use of these bodies, aluminium chloride and sulphate, zinc and magnesium chlorides, etc., in the treatment of cotton fabrics; as in finishing processes, where the goods are dried afterwards, there is a great liability to form hydrocellulose with the accompaniment of the tendering of the goods.

*Action of Acetic Acid on Cotton.*—As mentioned previously, dilute solutions of acetic acid have practically no effect on cotton. At temperatures of  $100^{\circ}$  C. and over, cellulose is converted by the action of glacial acetic acid and acetic anhydride into the mono-, di-, and tri-acetates. Acetyla-

tion of cellulose, however, is difficult. On the other hand, if acetylation is effected in the presence of a catalyst such as sulphuric acid or sulphuryl chloride, the reaction proceeds much more smoothly and at a lower temperature. According to the degree of acetylation, the product has varying solubility in organic solvents such as acetic acid, acetone, and chloroform.

Commercially, cellulose acetate is now being prepared in large quantities for conversion into artificial (Celanese) silk. This silk differs from other artificial silks in being a cellulose ester and not pure cellulose. On this account, it has dyeing properties different from those of cotton and these will subsequently receive special mention. On the other hand, the lustre and strength of acetate silk are excellent.

*Action of Nitric Acid.*—Very dilute nitric acid has but little effect on cotton. Concentrated nitric acid, preferably in the presence of sulphuric acid, readily converts cotton into esters—mono-, di-, or tri-nitrates—which are soluble in organic solvents and have important technical applications in the explosive and artificial silk industries. During nitration, the character of the cotton is fundamentally changed though it retains its fibrous structure.

*Action of Oxidising Agents on Cotton.*—Within limits, cellulose is not affected by oxidising agents such as bleaching powder, potassium bichromate, permanganate and hydrogen peroxide. If, however, the oxidation is more drastic, cellulose becomes profoundly affected, and is converted into what is generally known as oxycellulose. At present, our knowledge of this substance (or mixture of substances) is small, but of technical importance is the fact that cotton fabrics containing oxy-cellulose are weak, resist dyeing with direct cotton dyestuffs and have an abnormal affinity for basic dyes.

When cotton is dipped into strong solutions of bleaching

powder and then dried, it is found to be tendered very considerably—a fact which was first observed by the French chemist Witz.

In bleaching there is a great risk of the formation of oxycellulose if bleaching solutions of too great a concentration are used, or if the goods are subjected to too prolonged a bleaching treatment.

In bleached fabrics, the presence of oxycellulose may be detected by the following methods :—

- (1) Immerse the fabric in a solution of methylene blue, and then lightly rinse in water. The oxycellulose will be more deeply dyed than the remaining cotton.
- (2) Dye the fabric with sky blue FF. The oxycellulose will remain white.

(3) Boil the fabric in a solution prepared by adding, with shaking, a solution containing 4 grams of sodium thiosulphate, to a solution containing 1 gram of silver nitrate and subsequently adding 4 grams of caustic soda and diluting the whole to 100 c.c. The oxycellulose becomes stained dark brown, while normal cotton is almost unaffected.

Oxycellulose is partially soluble in caustic soda, but no method is known for reconverting oxycellulose into normal cellulose. It is, therefore, always advisable in carrying out any technical process connected with cotton, which involves its treatment with oxidising agents of any kind, and where it is desired not to damage the cotton, to shorten the treatment as much as possible.

**Solvents for Cotton.**—Although cellulose is insoluble in all the usual solvents, methods are known by which it can be dissolved to form viscous solutions from which, in most instances, the cellulose can be regenerated more or less in its original form.

One of the earliest known solvents for cellulose is a concentrated solution of zinc chloride which may be basic or

acidic. In either case, such a solution dissolves cellulose but slowly in the cold and it is therefore necessary to employ heat. On pouring this cellulose solution into water or alcohol, cellulose containing a certain amount of zinc is precipitated. At one time, artificial threads were made by this process, but this has long since been abandoned.

**Ammoniacal Copper.**—When ammonia is added to a solution of copper sulphate, there is formed at first a pale blue precipitate of copper hydroxide, which on adding excess of ammonia dissolves to a deep blue solution—a reaction highly characteristic of copper. The ammoniacal copper solution thus prepared has, as was first observed by John Mercer, the property of dissolving cellulose fairly rapidly, even in the cold. If instead of preparing the ammoniacal copper solution in the manner indicated above, which results in its containing a neutral ammonium salt, the copper hydroxide be prepared separately and then dissolved in ammonia, a solution is obtained which is stronger in its action. The cupro-ammonium solutions of cellulose are by no means stable but change on keeping. When freshly prepared, the cellulose may be precipitated from them almost unchanged by the addition of such bodies as alcohol, sugar and solutions of neutral alkaline salts. On keeping, the cellulose undergoes more or less hydrolysis or even oxidation, for it has been observed that oxycellulose is formed on prolonged digestion of cellulose with cupro-ammonium solutions. On adding lead acetate to the cupro-ammonium solution of cellulose, a compound of lead oxide and cellulose of somewhat variable composition is precipitated. It is of interest also to note that on adding metallic zinc to the cupro-ammonium solution the copper is thrown out and a solution containing zinc is obtained. The action of cupro-ammonium solutions on cellulose has been made the basis for the production of the "Willesden" waterproof cloths. Cotton cloths or paper are passed through

these solutions of various degrees of strength according to requirements, they are then passed between rollers which causes the surface to become more compact. There is formed on the surface of the goods a deposit of a gelatinous nature which makes the surface more compact, and the fabric becomes waterproof in character while the copper imparts to them a green colour and acts as a preservative against mildew. The "Willesden" fabrics have been found very useful for a variety of purposes.

Further, solutions of cellulose in cupro-ammonium solution are very largely employed for the manufacture of artificial silk. The process was started by Despaissis, a Frenchman, but it was subsequently largely developed by German interests. In the manufacturing process, cotton is dissolved in the ammoniacal solution of copper oxide, and then after filtration, it is squirted through fine jets into alkaline solutions, where the cellulose is immediately precipitated in the form of a flexible, rod-like filament. After thoroughly washing out the copper salts, this filament is dried and a lustrous silk substitute thereby obtained.

Cellulose is also soluble in certain proportions of caustic soda and carbon bi-sulphide. When cotton or wood pulp is steeped in caustic soda, then pressed so that its composition approximately agrees with the formula  $C_6H_{10}O_5 \cdot 2NaOH$ , and is then thoroughly agitated with carbon bisulphide, it passes into solution thereby forming what is known as viscose. By addition of water or acids to viscose, the cellulose is precipitated. Also, cellulose is regenerated when viscose is allowed to stand for several days. This peculiar property was discovered by Cross, Bevan, and Beadle, in 1892, and since then it has been largely applied in the manufacture of artificial silk and cellulose films. Such artificial silk of excellent quality is largely being made by Messrs. Courtaulds at Coventry and on the Continent.

**Dyes and Cotton Dyeing.**—An account of the chemistry

of the cotton fibre would be incomplete unless something were said about the reactions involved in the processes of dyeing and printing of cotton. This is a most interesting subject and opens up quite a number of problems relating to the combination of the fibre with colouring matter of various kinds, but will only be given here a brief outline of the principles on which the behaviour of the cotton fibre as regards colouring matter depends.

Having regard to the different affinities of dyes for cotton, there is (1) a large number of dye-stuffs called the Direct Cotton Dyestuffs—the Benzo, Congo, Diamine, Titan, Mikado, etc., dyes—that will dye the cotton from a plain bath or from a bath containing salt, sodium sulphate, borax, or similar salts ; (2) that there are dyes which, like Magenta, Safranine, Auramine and Methyl Violet, will not dye the cotton fibre direct, but require it to be mordanted or prepared with tannic acid ; (3) that there are some dyes which, like Alizarine, Nitrosoresorcine, Fustic, Logwood, etc., require alumina, chrome and iron mordants ; (4) that there are some dyes, acid wool dyes, comprising Azo Scarlet and azo colours in general, which cannot be used in cotton dyeing ; (5) that there are other dyes, *i.e.* vat and sulphur dyes, which do not come under this grouping.

The dyes used for colouring cotton may thus be classed into three main divisions :—

(1) *Direct Dyes*.—These are most important, since their method of application is so simple. Most of them are derived from benzidine, tolidine, and dianisidine. This class comprises some very fast and bright colours, and in many instances this fastness may be increased by suitable after-treatment. On the other hand, direct cotton dyes have an inferior brilliancy to basic dyes.

(2) *Mordant Dyestuffs*.—Such dyes are not used for cotton when they can be replaced by direct dyes, since their

application involves several processes which are costly. Generally, wool mordant dyestuffs are not used on cotton, except in special circumstances, such as in the production of turkey-red. On the other hand, basic dyes are largely used for cotton, the mordant used being almost always tannic acid which is further fixed by means of salts of antimony. Lately a tannin-substitute has been introduced under the name of Katanol, and since it behaves towards cotton as a direct dyestuff, it is very easy to apply. Generally, basic dyes on mordanted cotton yield bright shades which are of but moderate fastness to washing and light.

(3) *Vat and Sulphur Dyestuffs*.—These two classes of dyestuffs have the property of being insoluble in water or alkaline solutions except when in a reduced form. As reducing agents, sodium hydrosulphite and sodium sulphide are employed, the former for vat dyestuffs and the latter for sulphur dyestuffs. In dyeing, cotton is immersed in an alkaline solution containing the reduced dyestuff, and when absorption is complete, the cotton is exposed to the air or otherwise oxidised, whereby the absorbed dyestuff is converted into its original insoluble oxidised form within the fibres. Dyeings obtained with these dyestuffs are thus very fast to washing and generally to light and chemical reagents.

Finally, it may be mentioned that although about 1500 dyes are known and used, no satisfactory theory of dyeing has yet been evolved. The *chemical* theory assumes that dyeing involves the formation of a chemical combination of the cellulose with the dyestuff; the *mechanical* theory supposes that the cotton merely retains a dyestuff by mechanical absorption; a *solid solution* theory assumes that cotton acts as an organic solvent towards dyestuffs and the *absorption* theory involves the adhesive forces present in the cotton. Neither of these theories, however, is capable of explaining all the facts now known concerning the dyeing of cotton.

## CHAPTER II.

### BLEACHING, ETC., OF COTTON FABRICS PRIOR TO DYEING.

PREPARATORY to dyeing, it is necessary to prepare cotton, in whatever condition it is to be dyed—loose cotton, yarn, or piece—so as to bring it into a fit state to receive the dye and that the dyeing shall be properly accomplished. Raw cotton contains many mechanical and other impurities; cotton yarns gather dirt and various impurities during spinning; while in weaving it is practically impossible to keep the cloth clean, free from dirt, etc. Before cotton can be dyed a perfectly level and uniform shade free from dark spots or light patches, these impurities must be removed, and therefore the cotton is subjected to various scouring or cleansing operations with this end in view. Then again cotton naturally, especially Egyptian cotton, contains a small quantity of a *brown* colouring matter, and this would interfere with the purity of any pale tints of *blue, rose, yellow, green*, etc., with which the cotton may be dyed, and so this colour must be removed and the cotton rendered quite white. This is commonly called “bleaching.”

**Scouring Cotton.**—When dark shades—blacks, browns, olives, sages, greens, etc.—are to be dyed it is not necessary to bleach the cotton, but merely to scour it by boiling it with soda ash or caustic soda. This is very often carried out in the same machine as the goods will be dyed in; thus, for instance, in the case of pieces, they would be charged into a jigger, this would be filled with a liquor made from soda or

from caustic soda, and the pieces run from end to end, while the liquor is being brought to the boil—usually half to three-quarters of an hour is sufficient. Then the alkali liquor is run out, clean water run into the jigger, and the pieces washed, after which the dyes, etc., are run into the jigger and the dyeing done. There is usually used 2 lb. to 3 lb. of caustic soda, or 3 lb. to 4 lb. of soda ash for each 100 lb. of goods so treated. If the ordinary dyeing machines are not used for this purpose, then the ordinary bleachers' kairs may be used. These will be described later.

**Bleaching of Cotton.**—Cotton is bleached in the form of yarn, or in the finished pieces. In the latter case the method depends very largely on the nature of the fabric ; it is obvious that fine fabrics, like muslins or lace curtains, cannot stand the same rough treatment as a piece of twilled calico will. Then, again, the bleaching process is varied according to what is going to be done with the goods after they are bleached ; sometimes they are sent out as they leave the bleach-house ; again, they may have to be dyed or printed. In the first case the bleach need not be of such a perfect character as in the last case, which again must be more perfect than the second class of bleach. There may be recognised : (1) Market or white bleach. (2) Dyers' or printers' bleach. (3) Madder bleach. As (3) the madder bleach is by far the most perfect of the three, and practically includes the others, this will be described in detail, and differences between it and the others will be then pointed out. A piece is subjected to the madder bleach which has afterwards to be printed with alizarine colours. Usually in this kind of work the cloths are printed with mordant colours, and then dyed in a bath of the dyestuff. This stains the whole of the piece, and to rid the cloth of the stain where it has to be left white, it is subjected to a soap bath. Now, unless the bleach has been thorough, the whites

will be more or less stained permanently, and to avoid this cloths which are to be printed with alizarine colours are most thoroughly bleached. The madder bleach generally includes the following series of operations :—

- |                    |                  |
|--------------------|------------------|
| (1) Stitching.     | (6) Lye boil.    |
| (2) Singeing.      | (7) Resin boil.  |
| (3) Singeing wash. | (8) Wash.        |
| (4) Lime boil.     | (9) Chemicking.  |
| (5) Lime sour.     | (10) White sour. |

**I. Stitching.**—The pieces are fastened together by stitching into one long rope, which is passed in a continuous manner through all operations in which such a proceeding is possible. This stitching is done by machines, the simplest of which is the donkey machine, whereby the ends of the pieces, which are to be stitched together, are forced by a pair of cogwheels working together on to the needle carrying a piece of thread, this is then pulled through and forms a running stitch, a considerable length of thread being left on each side so as to prevent as far as possible the pulling asunder of the pieces by an accidental drawing out of the thread.

Sewing machines now used in bleach works are usually driven by power. The pieces are carried under the needle by a large wheel, the periphery of which contains a number of projecting pins that, engaging in the cloth, carry it along.

There is also a contrivance by which these pieces to be sewn can be kept stretched, this takes the form of an arm with clips at the end, which hold one end of the cloth while it is running through the machine. The clip arrangement is automatic, and just before the end passes under the needle it is released, and the arm flies back ready for the next piece ; it is, however, not necessary to use this arm always. This machine gives a chain-stitch sufficiently firm to resist a pull

in the direction of the length of the pieces, but giving readily to a pull at the end of the thread. The Rayer & Lincoln machine, an American invention, consists of a chain-stitch sewing machine mounted on the periphery of a large revolving wheel. This carries a number of pins, which, engaging in the cloth to be stitched, carry it under the needle of the machine. Besides sewing the pieces together this machine is fitted with a pair of revolving cutters which trim the ends of the pieces as they pass through in a neat, clean manner. There is also an arrangement to mark the pieces as they are being stitched. What is important in sewing the ends of pieces together is to get a firm uniform stitch that lies level with the cloths without any knots projecting, which would catch in the bleaching machinery during the processes of bleaching, and this might lead to much damage being done. Should it be necessary to mark the pieces so that they can be recognised after bleaching, the best thing to use is printers' ink. Gas tar is also much used, and is very good for the purpose. Coloured inks do not resist the bleaching sufficiently well to be used satisfactorily. Vermilion and Indian red are used for reds, yellow ochre is the fastest of the yellows, there is no blue which will stand the process, and Guignet's green is the only green that will at all resist the process, umber will serve for brown. All these colours are used with a printing ink vehicle.

The next operation is a very important one, which cannot be too carefully carried out, that is:—

**2. Singeing.**—For printing bleaches the cloths are singed. This has for its object the removal from the surface of the cloth of the fine fibres with which it is covered, and which would, if allowed to remain, prevent the designs printed on from coming out with sufficient clearness, giving them a blurred appearance. Singeing is done in various ways, by passing the cloth over a red-hot copper plate, or over a

red-hot revolving copper cylinder, or through a coke flame, or through gas flames. Plate singeing is the oldest of these methods and is still largely used. In this method a semi-cylindrical copper plate is heated in a suitable furnace to a bright red heat, the cloths are rapidly passed over it, and the loose fibres thereby burnt off. One great trouble is to keep the plate at one uniform heat over the whole of its surface : some parts will get hotter than others, and it is only by careful attention to the firing of the furnace that this can be obtained. To get over these difficulties Worral introduced a roller singeing machine in which the plate was replaced by a revolving copper roller, heated by a suitable furnace ; the roller can be kept at a more uniform temperature than the plate. The singe obtained by the plate and roller is good, the principal fault being that if the cloths happen to get pressed down too much on the hot plate the loose ends are not burnt off as they should be. With both plate and roller the cloths are singed only on one side, and if both sides require to be singed a second passage is necessary. Both systems still retain their hold as the principal methods in use, notwithstanding the introduction of more modern methods. Singeing by passing the cloths over a row, of Bunsen burners is now also universally used. This has the great advantage of being very cleanly, and of doing the work, very effectually, much more thoroughly than any other method, which is due to the fact that while in the methods described above only the loose fibres on the surface are burnt off, with gas all the loose fibres are burnt off. This is brought about by the gas flame passing straight through the cloth. It is not necessary to describe the gas singeing machine in detail. Singeing machines should be kept scrupulously clean and free from fluff, which is liable to collect round them, and very liable to fire. Most machines are fitted with a flue having a powerful draught which carries off this fluff. away

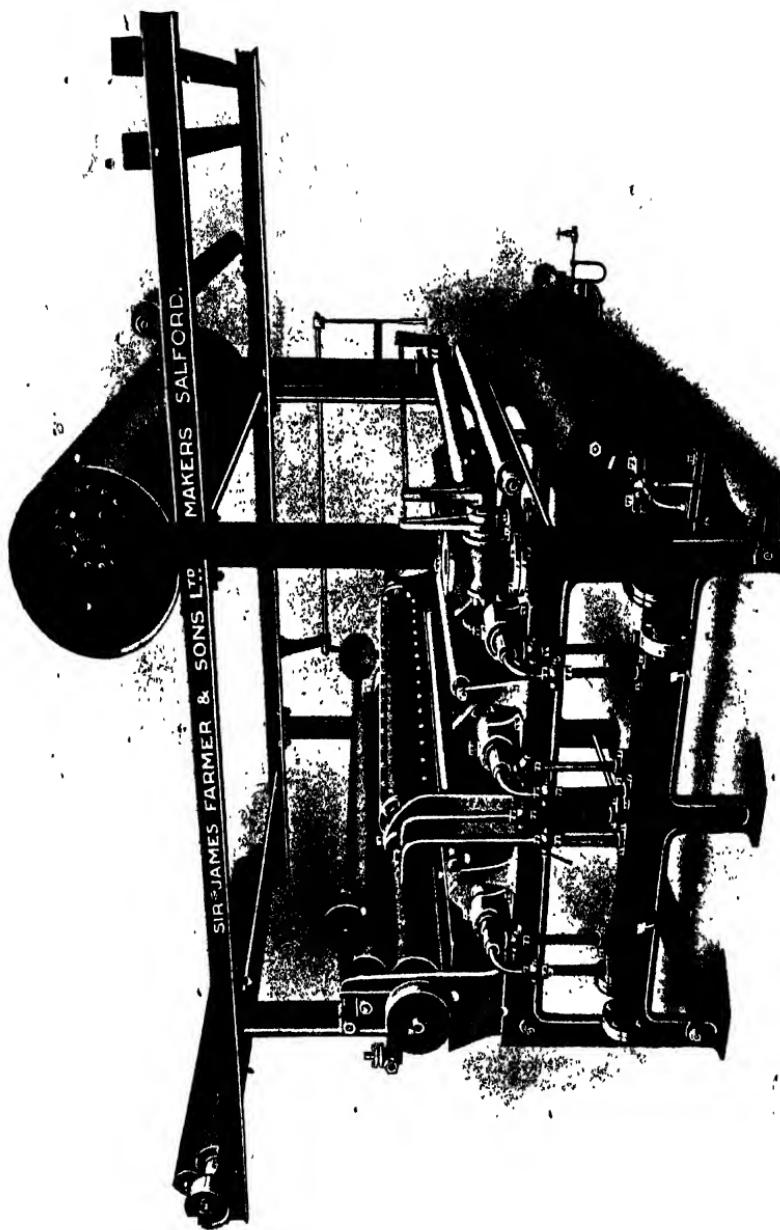
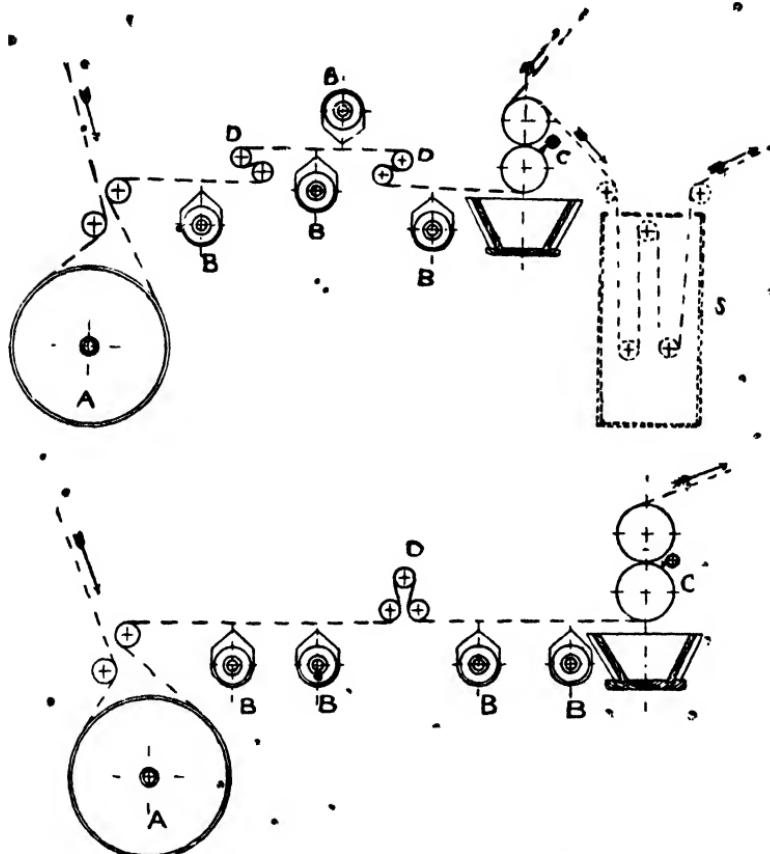


FIG. 4.—Modern gas singeing machine for cotton fabrics (Sir James Farmer, Norton, & Co. Ltd.).

from any source of danger. A modern gas singeing machine is shown in Figs. 4, 4A, 4B.

3. Singeing Wash.—After being singed the cloths are run through a washing machine to remove by water as much of



FIGS. 4A and 4B.—Path of fabric through singeing machine.

the loose charred fibres as possible. The construction of a washing machine is well known. It consists of a pair of large wooden rollers set above a trough containing water and into which a constant stream of water flows. In the trough is also fixed another wooden roller and the pieces are passed

round this bottom roller and between the top rollers. The cloth is passed through and round the rollers several times in a spiral form so that it passes through the water in the trough frequently, which is a great advantage, as the wash is thus much more effectual. The pressure between the two top rollers presses out any surplus water. The operation scarcely needs any further description.

4. **Lime Boil.**—After the cloth leaves the singeing or grey wash, as it is often called, it passes through the liming machine, which is made very similar to the washing machine. In this it passes through milk of lime, which should be made from freshly slaked lime. The latter may be prepared in a pasty form in a stone cistern. The lime used should be of good quality, free from stones, badly burnt pieces or any other insoluble material, so that when slaked it should give a fine smooth pasty mass. Lime should not be slaked too long before using, as it absorbs carbonic acid from the atmosphere, whereby carbonate of lime is formed, and this is useless for liming cloth. The pasty slaked lime may be mixed with water to form the milk of lime, and this can be run from the cistern in which it is prepared into the liming machine as it is required ; the supply pipe should be run into the bottom of the trough of the liming machine and not over the top, in which latter case it may splash on to the cloths and lead to overliming, which is not to be desired on account of its liability to rot the cloth. The amount of lime used varies in different bleachworks, and there is no rule on the subject ; about 5 lb. to 7 lb. of dry lime to 100 lb. of cloth may be taken as a fair quantity to use. The lime boil has for its object the removal or rather the saponification of the resinous and fatty matters present in the grey cloth, either naturally or which have been added in the process of weaving, or have got upon the cloth accidentally during the processes of spinning and weaving. With these bodies the lime forms insol-

uble lime soaps ; these remain in the cloth, but in a form easily decomposable and removable by treatment with acids and washing. Soda or potash is not nearly so good for this first boiling as lime—for what reason is somewhat uncertain, but probably because they form with the grease in the cloths soluble soaps, which might float about the keir and accumulate in places where they are not required and thus lead to stains, whereas the insoluble lime soap remains where it was formed. The lime also seems to attack the natural colouring matter of the cotton, and although the colour of the limed cloth is darker than before boiling, yet the nature of the colour is so altered that it is more easily removed in the after processes. Besides these changes the starchy matters put into the cloth in the sizing are dissolved away. Great care should be taken to see that the goods are evenly laid in the keirs, not too tight, or the liquor will not penetrate properly ; and not too slack, or they will float about and get entangled and more or less damaged. Then again care should be taken, especially when using low-pressure keirs, to see that the supply of liquor does not get too low, in which case the goods in the upper part of the keir are liable to get dry and are tendered thereby. So long as the goods in the keirs are not allowed to get dry there is no risk of damage. The inside of the keirs should be kept well limed, so that the goods shall not come in direct contact with the iron or metal of which the keir is constructed, as this would very likely produce stains which are by no means easy to remove. It is usual, and it is a good plan with almost all kinds of keirs, to put a number of large pebbles or small stones at the bottom of the keir, which serves to make a false bottom on which the goods rest and through which the liquor penetrates and flows away. Before use, the stones should be well washed to free them from dirt and grit. The lime boil is carried out in what are called “keirs.” Many forms of

keirs have been devised, but the one in most general use is that known as the "injector keir," of which drawings are given in Figs. 5, 6, 7, and 7A, of modern forms made by Messrs. Sir J. Farmer, Norton & Co., of Manchester. Injector kiers are made to work either under a pressure of 40 lb. to 50 lb.

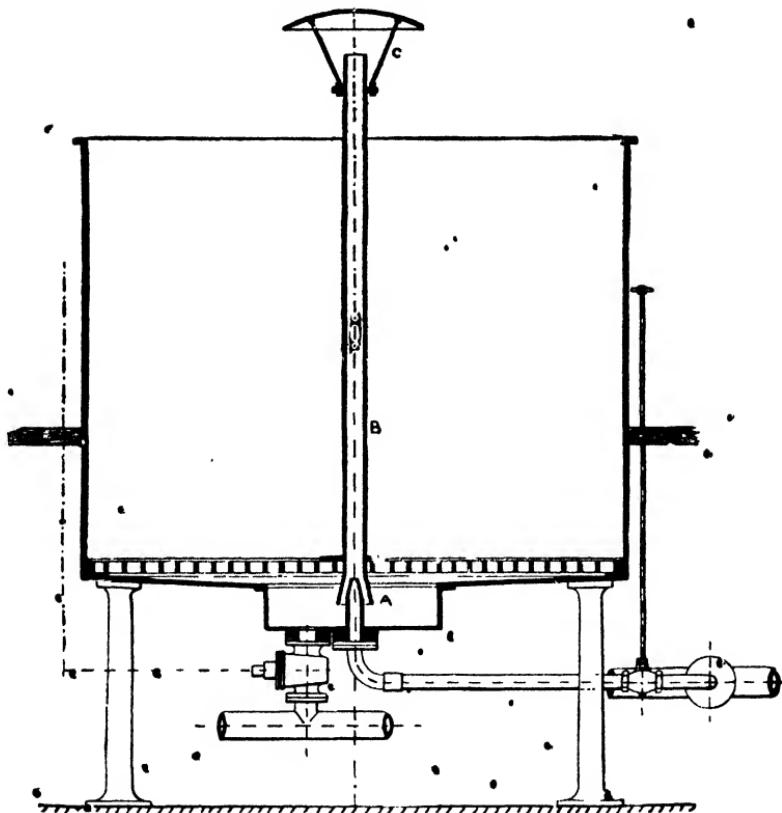


FIG. 5.—Section of low-pressure keir. (Sir James Farmer, Norton & Co. Ltd.)

of steam per square inch, when they are called high-pressure keirs, or at a pressure of 15 lb. to 20 lb., when they are called low-pressure keirs. The one shown in the drawing is intended for low-pressure keirs. The principle of construction is the same in all, the details varying somewhat with dif-

ferent makers. Injector kiers consist of a hollow, upright iron cylinder made of plates riveted together ; the top is made to lift off, but can be fastened down tightly by means of bolts and nuts, as shown in the drawing. From the

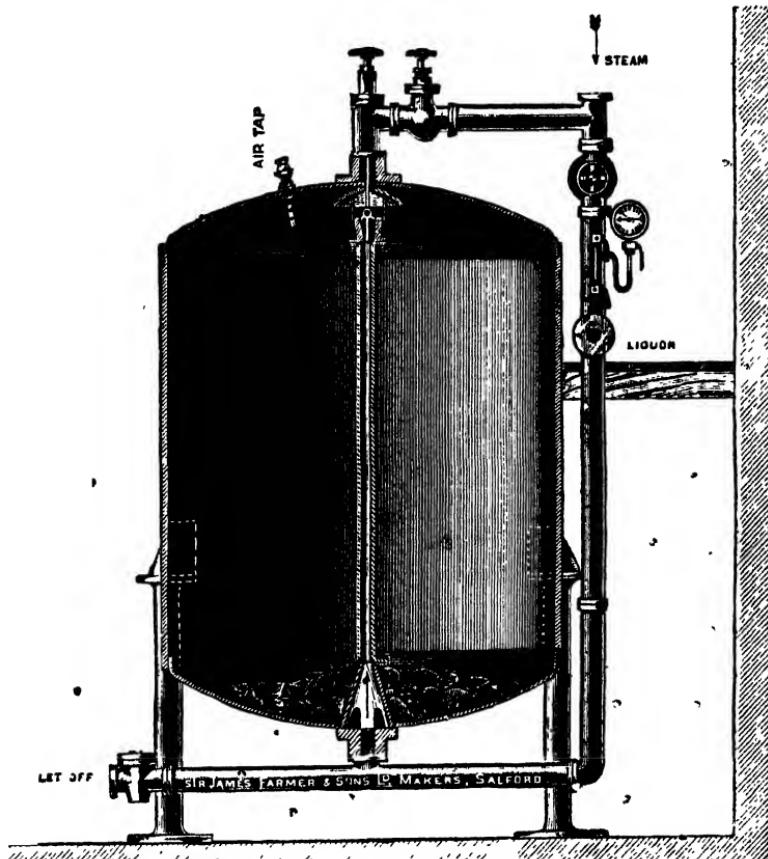


FIG. 6.—Section of high-pressure injector kier. (Sir James Farmer, Norton & Co., Ltd.)

bottom, and placed centrally, rises a pipe, known as the puffer pipe ; this terminates at the top in a rose arrangement. The lower end of the pipe is perforated. A jet of steam is sent in at the bottom of this pipe, and by its force any liquor

at the bottom of the keir is forced up the puffer pipe and distributed in a spray over any goods which may be in the keir. The liquor ultimately finds its way to the bottom of the keir ready to be blown up again. This circulation of the liquor can be maintained for any length of time and through its agency every part of the goods gets thorough and effectual treatment.

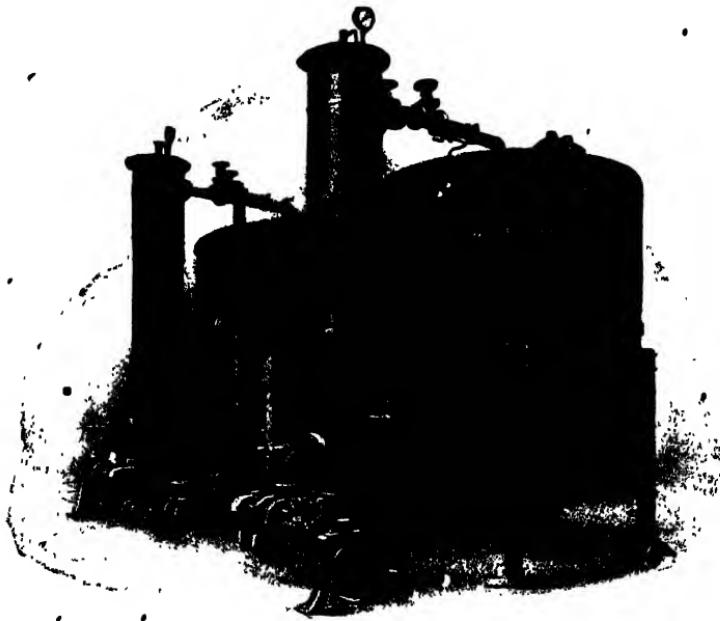


FIG. 7.—High-pressure kiers with multitubular heaters.  
(Sir James Farmer, Norton & Co., Ltd.)

The length of the boil depends upon the keirs ; with the open keir about ten hours are usually given, with injector keirs, working at a pressure of 40 lb. to 50 lb., six to seven hours are given.

**5. Lime or Grey Sour**—After the lime boil, the next operation is that of the lime sour or grey sour as it is often called to distinguish it from a subsequent souring. The souring is done in a machine constructed in the same way

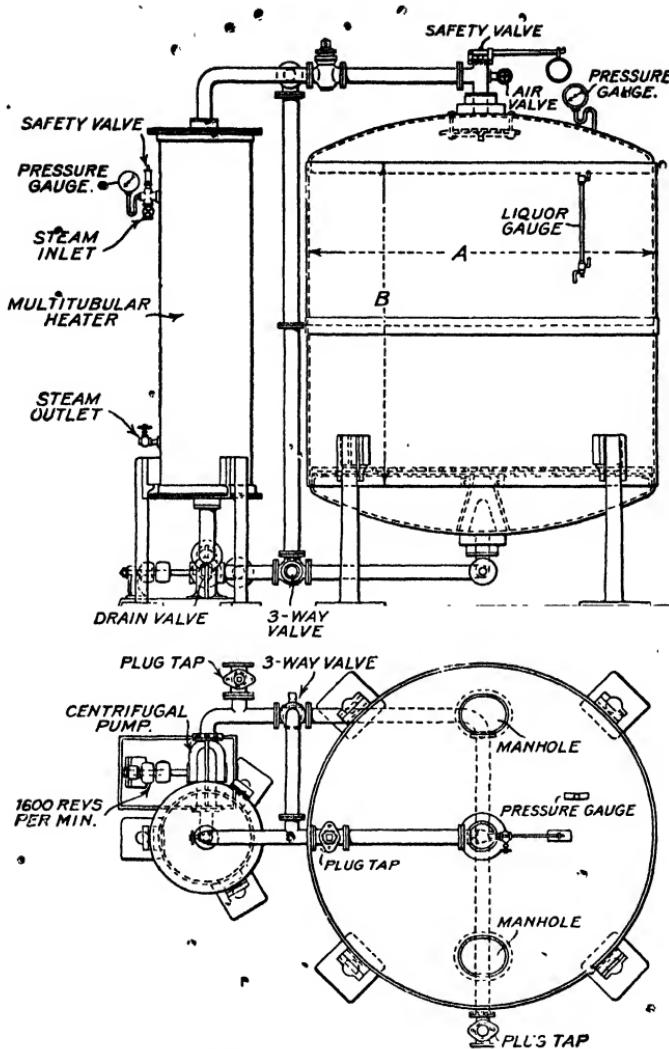


FIG. 7A.—Section of high-pressure kier with multitubular heaters.  
(Sir James Farmer, Norton & Co., Ltd.)

as a washing machine ; the trough of the machine is filled with hydrochloric acid at  $2^{\circ}$  Tw., specific gravity 1.016, which is kept ready prepared in a stone cistern and run into the

machine as required (it is not advisable to use acid stronger than this). After passing through the sour the goods are piled in a heap on the stillage for a few hours. The acid attacks the lime soap which was formed during the lime boil, decomposes it and dissolves out the lime with the formation of calcium chloride, while the fat of the soap is liberated, the former is washed away in the subsequent washing, while the latter remains to a large extent on the goods, and is removed by the lye boil that follows. Sulphuric acid is not so satisfactory to use for the lime sour as hydrochloric acid, because it forms insoluble sulphate of calcium with the lime which is difficult to entirely remove from the goods, whereas calcium chloride is very soluble and is entirely eliminated from the goods by the washing that follows. It is advisable to keep the acid at a uniform strength in the machine. The Twaddell is here of no use as an indicator of the actual strength, because, while the lime which the acid dissolves neutralises and reduces the strength of the acid, it actually raises the Twaddell, under which circumstance the only safe method is a chemical titration test.

After the souring it is often the custom to pile the goods on to a wooden stillage, but the goods should not be left too long so piled up for they may become dry, either entirely or in parts. In any case, as the goods dry the acid becomes concentrated and attacks them and makes them tender, which is not at all desirable. Therefore, if it is not convenient to proceed with them for some time after souring, they should be moistened with water from time to time, but it is best to wash them off at once, whereby they are made ready for the next operation.

6. **Lye Boil.**—This is, perhaps, the most important operation in the whole process of bleaching, especially if the cloths are going to be printed, in the so-called madder style with alizarin colours, or otherwise stains are liable to occur in the

final stage, and it is then sometimes difficult to put the blame for these upon the right shoulders. In principle the lye boil is simple, consisting in boiling the goods with a solution of soda ash or caustic soda. The quantity of ash used varies in different works, as might naturally be expected ; from 170 lb. to 200 lb. of ash to 10,000 lb. of cloth is a fair proportion to use. The length of boil averages about four hours, certainly not less than three should be given, and it is not necessary to give more than five hours in either ordinary keirs, with central puffer pipe, or in injector keirs. Care should be taken to see that the goods are well packed into the keirs, not too tightly or the lye will fail to penetrate equally all through, and this is important if a uniform bleach is desired ; neither should they be too loose, or they will float about and get torn. It is not necessary to be particular about the quantity of water used, except that it must be sufficient to keep the goods well covered, and still have enough to keep the circulation energetic. When the water is not sufficient in amount the goods get somewhat dry ; there is then a liability to tendering, but with plenty of water there is no fear of any damage being done during a boil with alkali. Some works use caustic soda instead of soda ash, in which case less is required, from 120 lb. to 150 lb. to 10,000 lb. of cloth, otherwise no alteration is made in the mode of boiling.

This lye boil clears away the fatty and waxy matter left in the goods after the lime sour, and thus prepares the way for the next boil. There is no advantage in using caustic soda in this preliminary boil, soda ash being just as effective and cheaper.

7. **Rosin Boil.**—Following the lye boil is the rosin boil which consists in boiling the goods in a rosin soap liquor. This is made as follows. A soda ash liquor of about 15° to 20° Tw. is prepared, and into this is thrown rosin, broken up into small pieces. The whole is boiled up until the rosin is

dissolved, and then as much more is added in small quantities as the alkali will dissolve. The soda liquor should not be much weaker than 20° Tw., it will then be heavier than the rosin which will float on the top ; it is found to dissolve quicker and better than when the liquor is weak, in which case the rosin would sink to the bottom of the boiler and would there melt into a single mass difficult to dissolve. The rosin soap liquor when made is ready to be used. The proportions of rosin and alkali used in the boil vary in different works, but, as a rule, the quantities for 10,000 lb. of goods are 430 lb. of 58 per cent. soda ash, 180 lb. of rosin, and 80 lb. of 70 per cent. caustic soda. Too much rosin should be avoided, as it is found that with an excess the whites obtained are not nearly so good as when the right quantity is used ; on the other hand, too little acts much in the same way. It may be taken that from  $1\frac{1}{2}$  to  $1\frac{3}{4}$  per cent. of the weight of the goods is about the right proportion ; 1 per cent. being too little, and 2 per cent. too much. The quantity of soda used should be rather more than twice that of the rosin, from  $3\frac{1}{2}$  to 4 per cent. The length of boil is usually about twelve hours in a low-pressure keir ; in a high-pressure keir about seven hours is sufficient. What the special function of the rosin is in this boil is not definitely known ; but experience, both on a large and small scale, proves that it is essential to obtaining a good white for alizarin printing ; without it, when the goods are dyed with alizarin after the mordants have been printed on, they frequently take a brown stain—with the rosin this never or but rarely happens.

8. **Wash.**—The goods must be washed after the lye boils, and it is important that this be done in as thorough a manner as possible. With the object of accomplishing this most thoroughly many washing machines have been invented, the main idea in all being to bring every part of the goods into contact with as much water as possible. A washing machine,

excellent in every respect, is shown in Fig. 8. It is made by Sir James Farmer, Norton & Co., Ltd., of Manchester.

9. **Chemicking.**—This is the actual bleaching operation, familiarly known as "chemicking," that is, the treatment of the goods with bleaching powder. The previous operations

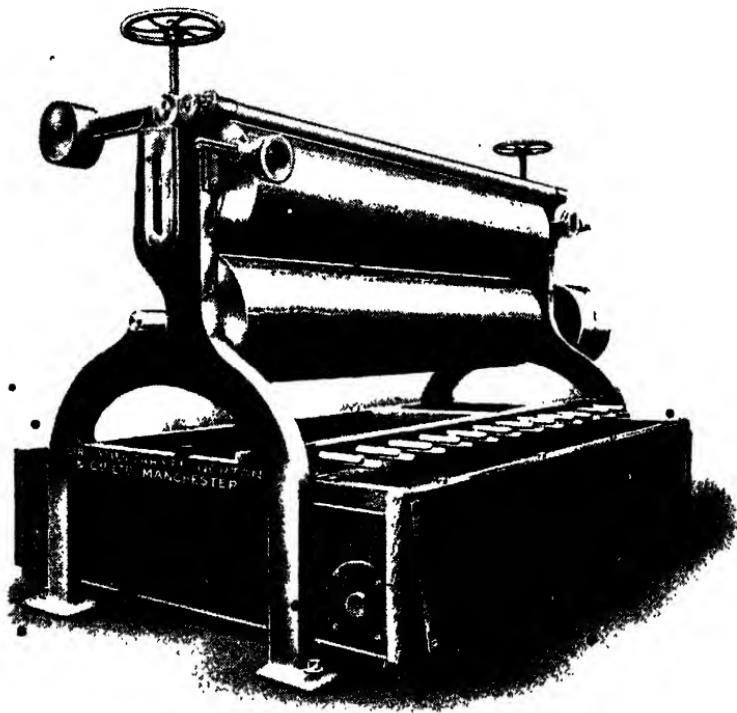


FIG. 8.—Bleach croft washing machine. (Sir James Farmer, Norton & Co. Ltd.)

have resulted in obtaining a cloth free from grease, natural or acquired, starch and from other impurities, but it still has a slight brownish colour. This has to be removed before the goods can be considered a good white, which it is the aim of every bleacher they should be. To get rid of this colour they

are subjected to some final operations, the first of which is now to be considered. The chemicking consists in running the goods through a weak solution of bleaching powder (chloride of lime), piling the goods up into heaps, and allowing them to lie overnight, the next day they are finished. As the cloth has received, or ought to have received, a thorough bottoming, only a weak bath of chemick is required, about  $\frac{1}{2}^{\circ}$  to  $1^{\circ}$  Tw. (sp. gr. 1.005 to 1.010) is quite sufficient. The solution is prepared in a stone cistern. There is very little difficulty in making it, the only precaution necessary is to have the solution quite clear and free from undissolved particles, for if these get upon the cloth they will either lead to the production of minute holes, or they may overbleach the fibre, which in such case will have the power of attracting excess of colour in any subsequent dyeing process and thus lead to stains, the origin of which may not be readily detected at the first sight. It is best, therefore, either to allow the solution to settle in the cistern till quite clear, which is the simplest way, or to filter through cloth. The chemicking is best done cold and with weak solution, at  $\frac{1}{2}^{\circ}$  Tw. (sp. gr. 1.005) rather than  $1^{\circ}$  Tw. (sp. gr. 1.010). Warming the liquor increases the rapidity of the bleaching action (it is found that the rate of bleaching is about doubled for  $7.5^{\circ}$  C. rise in temperature), but there is a risk of over-chloring, whereby oxycellulose is formed ; this must be avoided as far as possible, because the fibre is then tendered, moreover such over-chlored cloth has an affinity for basic colouring matters that is not at all desirable, as it leads to the production of stains and patches in the dyeing operations. It is preferable, when a single chemicking does not bleach the cloth sufficiently and give a white, to run the cloth twice through a weak liquor rather than once through a strong liquor. Although the chemicking is followed by a sour, which acting on the bleaching powder, liberates

chlorine that bleaches the fabric, yet the greatest proportion of the bleaching effect is brought about while the pieces are being piled up into heaps between the chemicking and the sour. In this state they should be left for some hours, covered over with a damp sheet, care being taken that they are not left piled so long as to become dry, as in this event there is a great risk of tendering the cloth or fabric ; it is, therefore, a good plan to moisten them with a little water from time to time. They should not be tightly piled up, but be as loose as possible, so that the air can get to them, as it is the carbonic acid and other acid vapours in the air that by acting on the chemick causes slow liberation of chlorine, which effects the bleaching of the goods.

Instead of bleaching powder, solutions of sodium hypochlorite are frequently used for bleaching. Also, bleach liquors prepared by directly bubbling chlorine gas in solutions of sodium carbonate or caustic soda are sometimes used. These solutions have the advantage of being more convenient to handle than bleaching powder, and, moreover, being free from suspended solids, there is no possibility of uneven or spotty bleaching.

For cotton bleaching, except under special circumstances, as in hosiery, peroxides such as hydrogen peroxide or sodium peroxide are not largely used.

**10. White Sour.** After chemicking the goods for which purpose either hydrochloric acid or sulphuric acid may be used. Hydrochloric acid possesses the advantage of forming a more soluble salt of lime (calcium chloride) than does sulphuric acid (calcium sulphate), and it has a greater solvent action upon any traces of iron and other metallic oxide stains which may be present in the goods. On the other hand, it is less pleasant to work with on account of its fuming properties. The souring is done by passing the goods through an acid liquor at 2° Tw. and piling for two

or three hours, after which it is washed. This final washing must be thorough, so that all traces of acid and chemick are washed out, otherwise there is a tendency for the goods to acquire a yellowish coloration. So far the routine has been described of the so-called madder bleach, the most perfect kind of bleach applied to cotton cloths. Besides this two other kinds of bleach are distinguished in the trade. Turkey red and market bleach. The former is used when the cloth or yarn is to be dyed plain or self-coloured with delicate shades with alizarin; the latter is used for cloth sold in the white. As the operations involved in producing these are identical in their method of manipulation to those already described, it will only be necessary to give an outline of the process for each one.

**Turkey Red Bleach.**—(1) Rinse through water into a keir and boil for two hours. (2) Lime boil for three to four hours. The amount of lime required is rather less than what is used with the madder bleach, from  $2\frac{1}{2}$  lb. to 3 lb. lime to each 1 cwt. of goods being quite sufficient. (3) Souring as in the madder bleach. (4) Lye boil, using about 100 lb. caustic soda to a ton of goods, and giving ten hours' boil. (5) Second lye boil, using about 50 lb. soda ash to a ton of goods, after which the goods are well washed. (6) Chemicking as with the madder bleach. (7) Souring as with the madder bleach, then washing well. This represents an average process, but almost every bleacher has his own methods, differing from the above in some of the details and this applies to all bleaching processes. It is obvious that the details may be varied to a great extent without changing the principles on which the process depends.

**Market Bleach.**—Here all that is necessary is to get the cloth of a sufficient degree of whiteness to please the eye of the customer. Market bleachers have, however, to deal with a wider range of goods than is dealt with in the former

kinds of bleaches, from very fine muslins to very heavy sheetings. Now it is obvious from a merely mechanical point of view, that the former could not stand as rough a process as the latter, therefore there must be some differences in the details of muslin bleaching and sheeting bleaching. Then, again, with goods sold in the white, it is customary to weave coloured headings or markings, and as these have to be preserved, to do so will cause some slight alteration of the details of the bleach with this object. On all these points it is difficult to lay down general rules because of the very varying feature of the conditions which are met with by the market bleacher. The rosin boil may be omitted, only two lye boils being required, and these need not be so long or of such a searching character as the corresponding boils of the madder bleach. Outlines of two or three such processes, which are now in use in bleachworks will serve to show the general routine of a market bleach. The proportions given are calculated for 10,000 lb. of goods.

(1) Lime boil, 500 lb. of lime, boil twelve hours. (2) Grey sour, hydrochloric acid of 2° Tw., specific gravity 1·010; wash well. (3) Lye boil, 100 lb. caustic soda, 70 per cent. solid boil ten to twelve hours; wash. (4) Second lye boil, 100 lb. 58 per cent. soda ash, boil twelve hours. (5) Chemick bleaching powder liquor at 1° Tw. (sp. gr. 1·005), boil for three hours; wash. (6) White sour, sulphuric acid at 2° Tw. specific gravity 1·010; wash well. The length of boil with the lime and lyes depends upon the quality of the goods heavy goods require from two to three hours longer than light goods, such as cambrics, the time given above being that for heavy goods, sheetings, etc. Another process is the following. (1) Lime boil, 480 lb. lime, boil for ten hours (2) Grey sour, hydrochloric acid at 2° Tw. (sp. gr. 1·010) wash. (3) Lye boil, 300 lb. soda ash, 58 per cent.; 50 lb

caustic soda, 70 per cent., and 30 lb. soft soap, boil ten hours ; wash. (4) Chemick as above. (5) White sour as above ; wash well. A smaller quantity of lime is used here, but the lye boil is a stronger one. This process gives good results. Some bleachers do not use lime in their market bleaches, but give two lye boils.

(1) Lye boil, using 140 lb. caustic soda, of 70 per cent., boil ten hours ; wash well. (2) Second lye boil, 120 lb. soda ash, 58 per cent., boil ten hours ; wash. (3) Chemick as above. (4) White sour as above ; wash well. Light fabrics, such as laces, lace curtains, muslins, etc., cannot stand the strain of the continuous process, and they are, therefore, subjected to a different bleaching process, which varies much at different bleachworks. One method is to lime by steeping for an hour in a weak lime liquor, using about 2 lb. of lime to 100 lb. of goods ; they are then boiled in the keir for eight hours, after which they are washed. This washing is done in what are called dash wheels, large hollow wheels, the interior of each being divided into four compartments. Into these the goods are put, and the wheel is caused to revolve, while at the same time a current of water flows with some force into the interior of the wheel and washes the goods. The dash wheels do their work well, and the action being gentle the finest fabrics can be washed without fear of any damage. It is necessary that the speed at which they are driven should be such that as the wheel revolves the goods are thrown from side to side of each compartment ; if the speed be too slow they will simply slide down, and then they do not get properly washed ; on the other hand, if the speed be too great then centrifugal action comes into play and the goods remain in a stationary position in the wheels with the same result. As to the amount of washing, it should be as before. After this washing they are boiled again in the keir with soda ash, using about 8 lb. ash for 100 lb. goods,

and giving seven hours' boil, which, after washing, is followed by a second boil with 5 lb. ash and 4 lb. soft soap for each 100 lb. of goods, giving eight hours' boil. They are then washed and entered into the chemick. The chemicking is done in stone cisterns, which are fitted with false bottoms, on which the goods can rest, and which allow any insoluble particles of bleaching powder to settle out and prevent them from getting on the goods. The liquor is used at the strength of about  $\frac{1}{2}^{\circ}$  Tw. (sp. gr. 1.0025), and the goods are allowed to steep about two hours; they are then placed in a hydro-extractor, and the surplus chemick is whizzed out, after which they are steeped in sour of hydrochloric acid at  $1^{\circ}$  Tw., kept in a stone cistern, the goods being allowed to steep for two hours. Next they are washed, well whizzed, passed through a blueing water, whizzed again, and dried. The remarks made when describing similar operations of the madder bleach as to the action, testing, etc., of the chemicals, are equally applicable here.

Another method of bleaching fine fabrics is shown in outline in the following scheme. (1) Wash; boil in water for two hours. (2) Boil in soda for five hours, using 80 lb. 58 per cent. soda ash, and 30 lb. soft soap for 1000 lb. of goods. (3) Second soda boil, use from 40 lb. to 50 lb. soda ash, and 15 lb. to 20 lb. soft soap, boil four hours; after each soda boil the goods should be washed. (4) Chemick, using bleaching powder liquor at  $\frac{1}{2}^{\circ}$  Tw., specific gravity 1.0025, allowing them to steep for two hours, then wash and whiz. (5) White sour, using hydrochloric acid at  $2^{\circ}$  Tw. specific gravity, steeping two hours; wash. A further extension of the same process is sometimes given for the best goods, which consists, after the above, in giving: (6) A third soda boil, using 25 lb. to 30 lb. soda ash and 15 lb. to 20 lb. soft soap, giving boil one hour; wash. (7) Chemick as before. (8) Sour as before, after which the goods are well washed.

Within recent years, the use of enzymes in the treatment of fabrics has been continuously improved, so that to-day huge quantities of diastase are employed for removing starchy impurities from fabrics where it is undesirable that they should undergo the normal processes of bleaching and scouring.

Such products are usually prepared by fermentation of barley or rice and contain an enzyme known as *diastase* which has the property of rapidly liquefying starch. Many

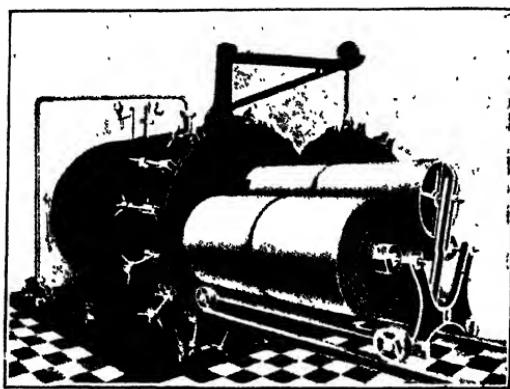


FIG. 9.—Open width bleaching kier. (Jackson & Brother, Ltd.)

such preparations are on the market and they are usually of a reliable quality. They are usually employed after the operation of singeing. The singed fabric is run through a bath containing about 1 lb. of diastase in 40 gallons of water, and is then allowed to steep overnight. Subsequently the fabric is then thoroughly washed, whereby liquefied starch and other loosened impurities are removed, so that the fabric may then be lightly scoured or bleached and is thus ready for dyeing or other treatment. Diastase preparations have no deleterious action on cotton whatever.

A further improvement in the bleaching of fabrics deserves mention. It will be readily seen that when fabrics are bleached and subjected to keir boiling in rope form, there is the possibility that permanent creases or derangement of the woven yarn may arise. Such creases may persist even after subsequent dyeing. For this reason, keirs have been devised in which fabrics may be bleached in open width. The Jackson keir is of this type and is shown in Fig. 9.

In the Jackson keir, the fabric is automatically wound, in either direction, from one roller to another under tension and in open width, while the hot caustic liquors are circulated through the fabric. The treatment of the fabric is thus very effective and the results are excellent. By this method, keiring may be accomplished at ordinary or increased pressures.

**Yarn Bleaching.**—Yarn is supplied to the bleacher in two forms: (1) warps in which the length of the threads may vary from as little as 50 to as much as 5000 yards; these can be dealt with in much the same manner as a piece of cloth, that is, a continuous system can be adopted; (2) hanks, which are too well known to require description. Often, yarn is bleached in the form of cops, though the results of cop bleaching are not so satisfactory.

**Warp Bleaching.**—The warp, if very long, is doubled two, three, or four times upon itself, so as to reduce its length. Care should be taken that the ends of the warp are tied together to prevent any chance of entangling, which would very likely happen if the ends were left loose to float about. As a rule, warps are not limed, but the adoption of liming would assist the bleaching. In outline warp bleaching consists of the following operations: (1) Lye boil, using 30 lb. caustic soda, 70 per cent., and 50 lb. soda ash, 58 per cent., giving six hours' boil, and washing. (2) Sweeting, boil with

30 lb. soda ash, 58 per cent., for two hours. (3) Washing. (4) Chemicking, bleaching powder liquor at 1° Tw., washing. (5) Sour, sulphuric acid at 2° Tw., washing well. (6) Hydro extracting and drying. About 2000 to 3000 lb. of warps are usually treated at one time. The machinery used may be the same as that used in the cloth bleach, and each operation may be conducted in the same manner. In some warp bleach-works, while the keirs are made in the same way, the other machines are made differently. The chemicking and souring is done in strong cisterns provided with a false bottom; in these the warps are allowed to remain for about two hours. A more complicated form of chemicking cistern is also in use. This is made of stone, and is provided with a false bottom. Above is a tank or sieve, as it is called, having a perforated bottom through which the liquor flows on the warp in the cistern below. Under the chemicking cistern is a tank into which the liquor flows, and from which it is pumped up into the sieve above. A circulation of liquor is thus kept up during the whole of the operation. Owing to the action of the chemick or acid on the metal work of the pump there is great wear and tear of the latter, necessitating frequent repairs. This is a defect in this form of chemicking machine. For drying the warps a hydro-extractor is first used to get the surplus liquor from the goods. This machine is now well known, and is in use in every bleachworks, where it is familiarly known as the "whiz," and the operation is generally called whizzing. Hydro-extractors are described under the head of "Dyeing Machinery." The actual drying of the warps is done over the "tins" as they are called. These are a number of large cylinders measuring about 20 inches in diameter and about—for warp drying—5 feet long. Usually they are arranged vertically in two tiers, each tier consisting of about five cylinders, not arranged directly one above another but in a zig-zag manner, the centres of the first, third,

and fifth being in one line, and the centres of the others in another line. The cylinders are made to revolve by suitable driving mechanism, and into them is sent steam at about 5 lb. to 10 lb. pressure, which heats up the cylinders, whereby the warp passing over them is dried. This drying may be partial or complete, being regulated by the speed at which the warps pass over the cylinders and by the quantity of steam passed into the same. The quicker the speed and the smaller the amount of steam, the less the warps are dried ; while, on the other hand, the slower the speed and the larger the amount and greater the pressure of the steam, the quicker and more thoroughly are the warps dried. As there is a great deal of water formed in the cylinders by the condensation of the steam, means are always provided for carrying off this water, as its retention in the cylinders often leads to serious results and damage to the machine.

**Hank Bleaching.**—So far as the chemical part of hank bleaching is concerned it does not differ from that of warp bleaching ; the same operations and proportions of chemicals may be used and in the same order, but there is some difference in the machinery which is used. The hanks may be manipulated in two ways : they may be either kept in separate hanks, which is the method mostly in vogue in modern bleach-houses, or they may be linked together in the form of a chain. In the latter case the operations and the machinery may be the same as used in the madder bleach, with a few unimportant minor differences. In the final washing the bumping machine is used, which consists of two wooden bowls set over a wooden trough containing the wash waters. The top bowl is covered with a thick layer of rope and merely rests on the bottom bowl by its own weight, and is driven by friction from the latter. The chain of hanks passing through between the two bowls has the surplus liquor squeezed out of it, and as there is considerable increase in the thickness

at the points of linkage between the hanks, when these pass through the bowls they lift up the top bowl, which, when the thick places have passed through, falls down with a sudden bump upon the thin places, and this bumping drives out all the surplus liquor and drives the liquor itself into the very centre of the hanks, which is sometimes an advantage. In modern bleach-houses the chain form is giving place to the method of bleaching separate hanks, partly because so many improvements have been made in the hank-bleaching machinery of late years, which enables bleachers to handle the yarn in the form of separate hanks better than they could do formerly; and as bleaching in separate hanks means that the cotton is kept in a more open form, and is thus more easily penetrated by the various liquors which are used, it follows that the bleach will be better and more thorough, which is what the bleacher aims at. At the same time weaker liquors or, what is the same thing, less material can be used, which means a saving in the cost of the process. For bleaching yarn in the hank the following process may be followed with good results. (1) Lye boil, using 1000 lb. yarn, 40 lb. caustic soda of 70 per cent., and 50 lb. of soda ash of 58 per cent., giving five to six hours' boil at low pressure. (2) Wash through washing machine. (3) Second lye boil, using 40 lb. soda ash of 58 per cent., and giving two to three hours' boil, wash again through a washing machine. (4) Chemick as in warp bleaching. (5) Sour as in warp bleaching. (6) Wash well. (7) Hydro-extract and dry. Sometimes, if the yarn is to be sold in thread form, before the last operation it passes through another, *viz.* treating with soap and blue liquors, which will be dealt with presently. The lye boils are done in the ordinary keirs, and do not call for further notice, except that in filling the goods into the keirs care should be taken that while sufficiently loose to permit of the alkaline liquors penetrating through

the hanks properly, yet they should be so packed that they will not float about and thus become entangled and damaged. The washing is nowadays done in a special form of washing machine, designed to wash the hanks quickly and well with as little expenditure of labour and washing liquor as possible. There are now several makes of these washing machines on the market, most of them do their work well, and it is difficult to say which is the best. Some machines are made to wash only one bundle at once, while others will do several bundles. Generally the principle on which they are constructed is the same in all, a trough containing the soda ash liquor, over which is suspended a revolving reel or bobbin, usually made of wood or enamelled iron, the bobbin being polygonal in form so that it will overcome readily any resistance the yarn may offer and carry the hank round as it revolves. The hank dips into the wash liquor in the trough, and as it is drawn through by the revolution of the bobbin it is washed very effectually. The moving of the hank opens out the threads, and thus the wash liquor thoroughly penetrates to every part of the hank, so that a few minutes' run through this machine thoroughly washes the yarn. A constant stream of clean water is passed through the trough. This machine may also be used for soaping and sizing the hanks if required. By extending the trough in a horizontal direction, and increasing the number of reels or bobbins, the quantity of material that can be washed at one time can be extended, although not to an indefinite extent. The workman can start at one end of the machine and fill all the bobbins with yarn; by the time he has finished this the first bobbinful will have been washed sufficiently and can be taken off and replaced with another quantity of yarn, and thus one by one the bobbins may be emptied and refilled, which means that a considerable amount of material can be got through in the course of a day. To avoid the labour of

walking to and fro to fill and refill the bobbins, washing machines are constructed in which the trough is made in a circular form. The bobbins are placed at the ends of radial arms which are caused to revolve round over the trough, the workman is stationed constantly at one part of the circle, and as the arms pass him in their motion round the trough

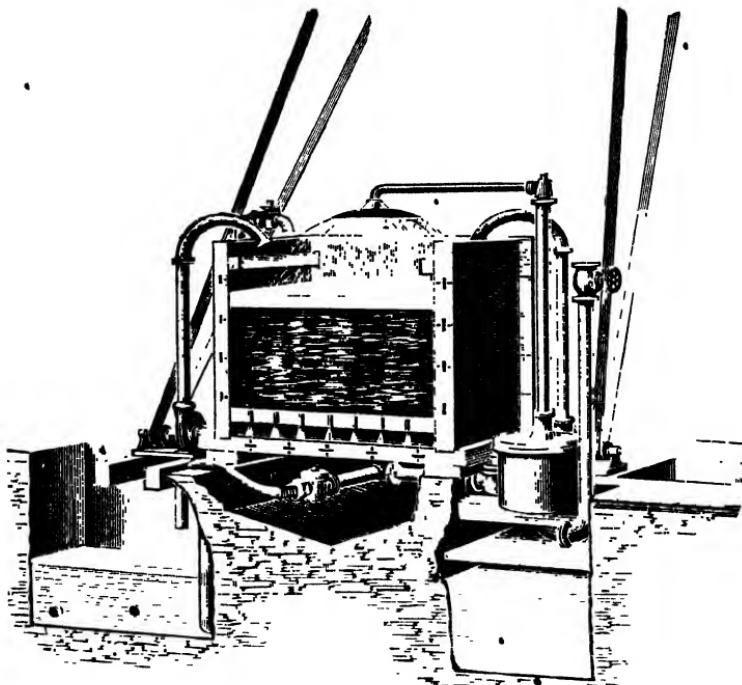


FIG. 10.—Mather & Platt's yarn-bleaching kett.

he takes off the washed hanks and puts on the unwashed hanks. By this machine he is saved a very considerable amount of labour, and is able to do his work in a more convenient manner. The yarn is well washed in such a machine. The trough may be entire or it may be divided into a number of compartments, each of which may contain a different kind

of wash liquor if necessary. Of course, it goes almost without saying that in all these machines the liquors in them may be heated up by means of steam pipes if required. The chemicking and souring of the hanks does not call for special mention, beyond the fact that these operations are done in the same manner as warp bleaching. In Fig. 10 is shown Mather & Platt's yarn-bleaching keir, which is designed to bleach cotton yarn, either in hanks or in the warp forms, without removing it from the vessel into which it is first placed. The process is as follows : The hot alkali solution is circulated by means of a distributing pipe through the action of an injector or centrifugal pump to scour the yarn ; then water is circulated by means of a centrifugal pump for washing. The chemick and sour liquors are circulated also by means of pumps, so that without the slightest disturbance to the yarn it is quickly and economically bleached.

*Stains and Damages to Bleached Goods.*--Some of the stains in bleached goods which are met are beyond the control of the bleacher to avoid, while others are due to various defects in the process. Now the subject of stains can only be dealt with in a very general way, because of the varying manner in which they arise. The recognition of the particular way in which the stains have been formed is sometimes difficult to discover. First, there are iron stains, which are the most common kind of stains that a bleacher is troubled with. These generally make their appearance in the form of red spots of greater or less extent. As a rule they are not visible before the pieces are fully bleached. Their origin is varied. Sometimes they arise from the machinery ; if the keirs are not kept thoroughly whitewashed out, there is a great liability to produce iron stains. Every other machine which is used in the process is made of iron, and should be kept free from rust, or the chances of stains are considerably increased. The water used in the bleaching

must be free from iron. A small trace will not make much difference, but some waters contain a great deal of iron, so much so that they are absolutely unusable for bleaching purposes. Iron stains are often due to a very curious cause : the dropping of the oil used in the spinning or weaving machinery on to the cotton during the process of manufacture. This oil is often charged with iron derived from the wear and tear of the machinery, and which often gets fixed in the form of red spots of oxide on the fibre. Iron stains can usually be removed by treatment with oxalic acid. Oil stains are also common. These take the form of bright yellow stains in various shapes, sometimes extending along the piece in streaks, at other times in patches in various places about the piece. Generally these oil stains do not make their appearance as soon as the piece is bleached, and often the bleacher sends out his goods quite white and apparently all right, and yet soon afterwards comes a complaint that the goods are stained yellow. One cause of these yellow oil stains can be traced to the use of paraffin wax in the sizing of the warps. In this case the stains are more or less streaky in form, and extend along the length of the piece. They are due to the fact that paraffin wax is not saponifiable by the action of the alkalis used in the process, and is therefore not extracted. When the goods are chemicked the chlorine acts upon the paraffin and forms chlorine compounds, which are acted upon by light, and turn yellow by exposure to that agent and to the atmosphere. Paraffin, when used for the sizing of warps, may sometimes be completely extracted from the fabric, but this depends upon the proportion of tallow or other fat which is used in the composition of the sizing grease. If the paraffin is only present in small quantities, and the grease well mixed, then it may be possible to extract all the paraffin out of the fabric during the bleaching process, but if the paraffin is in large proportion, or the grease

not well mixed, it is scarcely possible to extract it all out, and stains must be the result. These stains can hardly be considered the fault of the bleacher, but are due to the manufacturer of the cloth using cheap sizing compositions on his warps. There are no means which can be adopted before bleaching to ascertain whether paraffin exists in the cloth. If found to be present, the remedy which is the easiest practically is to saturate the cloth with a little olive oil, or better, pale oleic acid. Allow the fatty matter to soak well in, and then boil the goods in a little caustic soda. Another cause of oil stains is the use of mineral oils in the lubrication of cotton machinery. These mineral oils partake of the nature of paraffin in their properties, and, therefore, they are unsaponifiable by the action of alkalis. Like paraffin wax, they resist the bleaching process, and much in the same manner produce stains. Oil stains show themselves in various forms—sometimes as spots. These may be due to the splashing of oil from the spindles during the process of spinning, or they may be in patches of a comparatively large size over the pieces.

These are perhaps due to the oil dropping on to the piece during the process of weaving when in the loom. The oils used for the lubrication of spinning and weaving machinery should contain a fair proportion of some fatty oil, such as olive or rape or coconut oil. Not less than 10 per cent. should be used. More would be better, but the cost, of course, would be greater and oil is an item with spinners and manufacturers. Isolated oil stains in fabrics may be frequently easily removed by sponging the fabric with an organic solvent such as benzene, alcohol, etc.

Stains are occasionally due to other causes. Their production is frequently spasmodic and under circumstances such that the cause is difficult to trace. The presence of stains is often not apparent during the bleaching process, but

only after dyeing or printing. But, however produced or whatever their appearance, stains should be investigated so that it may be established whether (1) mineral or organic impurities are present, or (2) the cotton is chemically affected. If impurities are present, they can usually be identified by the usual methods of chemical analysis and their origin discovered. If the cotton is affected, the action of acids, oxidants, or alkalis may be suspected; usually such affected cotton contains oxycellulose and this may be detected by the methods already described.

The damages liable to occur in the bleaching of cotton are dealt with very exhaustively in Tailfer's "Bleaching of Linen and Cotton Yarn and Fabrics" (Second Edition. Scott, Greenwood & Son). The apparatus used in the singeing of cotton prior to bleaching is also fully illustrated and described therein.

## CHAPTER III.

### DYEING MACHINERY AND DYEING MANIPULATIONS.

COTTON is dyed in a variety of forms : raw, loose cotton, partly manufactured fibre in the form of slubbing or sliver, spun fibres or yarns wound in cop or bobbin forms, in hanks or skeins and in warps, and lastly in the form of woven pieces. These different forms necessitate the employment of different forms of machinery and different modes of handling ; it is evident to the least unobservant that it would be quite impossible to subject slubbing or sliver to the same treatment as yarn or cloth, otherwise the slubbing would be destroyed and rendered valueless. In the early days all dyeing was done by hand in the simplest possible contrivances, but during the last quarter of a century there has been a great development in the quantity of dyeing that has been done, and this has necessitated the application of machinery, for hand work could not possibly cope with the amount of dyeing now done. Consequently there has been devised during the past two decades a great variety of machines for dyeing every description of textile fabrics ; some have not been found a practical success for a variety of reasons and have gone out of use, others have been successful and are in use in dyeworks.

*Hand Dyeing.*—Dyeing by hand is carried on in the simplest possible appliances ; much depends upon whether the work can be done at the ordinary temperature or at the boil. Figs. 11A and 11B show respectively a rectangular vat and a round tub much in use in dye-houses. These are made

of wood, but copper dye-vats are also made. These may be used for all kinds of material, loose fibre, yarns or cloth. In the case of loose fibre this is stirred about either with poles

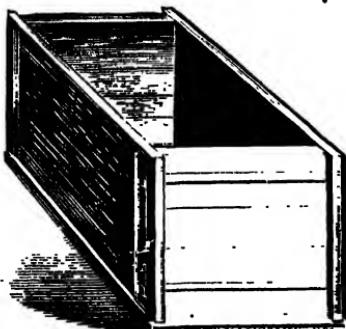


FIG. 11A. -Rectangular dye-tank.

or with rakes, care being taken to turn every part over and over and open out the masses of fibre as much as possible in order to avoid matting or clotting together. In the case of

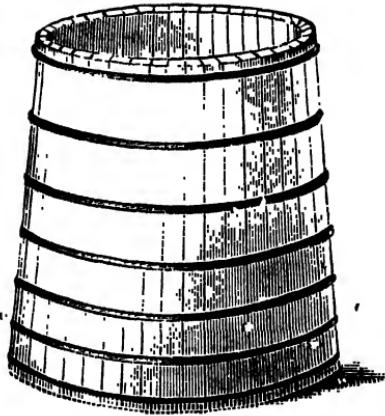


FIG. 11B. -Round dye-tub.

yarns or skeins, these are hung on sticks resting on the edges of the tub or vat. These sticks are best made of hickory, but ash or beech or any hard wood that can be worked smooth

and which does not swell much when treated with water may be used. The usual method of working is to hang the skein on the stick, spreading it out as much as possible, then immerse the yarn in the liquor, lift it up and down two or three times to fully wet out the yarn, then turn the yarn over on the stick and repeat the dipping processes, then allow to steep in the dye-liquor. This is done with the batch of yarn that is to be dyed at a time. When all the yarn has been entered into the dye-bath, the first stickful is lifted out, the yarn turned over and re-entered in the dye-liquor; this operation is carried out with all the sticks of yarn until the cotton has become dyed of the required depth. In the case of long rectangular vats it is customary for two men, one on each side of the vat, to turn the yarns, each man taking charge of the yarn which is nearest to him. The turning over one lot of yarn is technically called "one turn," and the dyer often gives "three turns" or "four turns" as may be required. Woven goods may be dyed in the tub or vat, the pieces being drawn in and out by poles, but the results are not altogether satisfactory and it is preferable to use machines for dyeing piece goods. Plain tubs or vats, such as those shown in Figs. 11A and 11B, are used for dyeing, and otherwise treating goods in the cold, or at a lukewarm heat, when the supply of hot water can be drawn from a separate boiler. When, however, it is necessary to work at the boil, then the vat must be fitted with a steam coil. This is best laid along the bottom in a serpentine form. Above the pipe should be an open lattice-work bottom, which, while it permits the free circulation of boiling water in the vat, prevents the material being dyed from coming in contact with the steam pipe. This is important if uniform shades are to be dyed, for any excessive heating of any portion of the bath leads to stains being produced on the material in that part of the bath. Fig. 12 shows a vat fitted with a steam pipe. That portion of the steam pipe which

passes down at the end of the vat is in a small compartment boxed off from the main body of the vat, so that no part of the material which is being dyed can come in contact with it. A closed steam coil will, on the whole, give the best results, as then no weakening of the dye-liquor can take place through dilution by the condensation of the steam. Many dye-vats are, however, fitted with perforated, or, as they are called, open steam coils, in which case there is, perhaps,

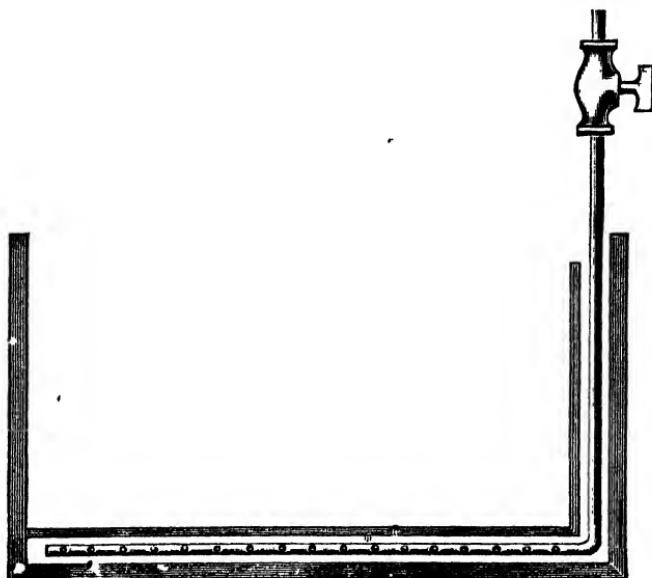


FIG. 12. Section of dye-vat.

better circulation of the liquor in the dye-vat, but as some of the steam must condense, there is a little dilution of the dye-liquor in the vat.

**Dyeing Machines.**—Dye-tubs and vats, such as those described above, have been largely superseded by machines in which the handling or working of the materials being dyed is effected by mechanical means. There have been a large number of dyeing machines invented; some of these have not

been found to be very practical, and so they have gone out of use. Space will not admit of a detailed account of every kind of machine, but only of those which are in constant use in dye-works.

*Dyeing Loose, or Raw Cotton.*

**Delahunty's Dyeing Machine.**—This is illustrated in Fig. 13. It consists of a drum made of lattice work, which can

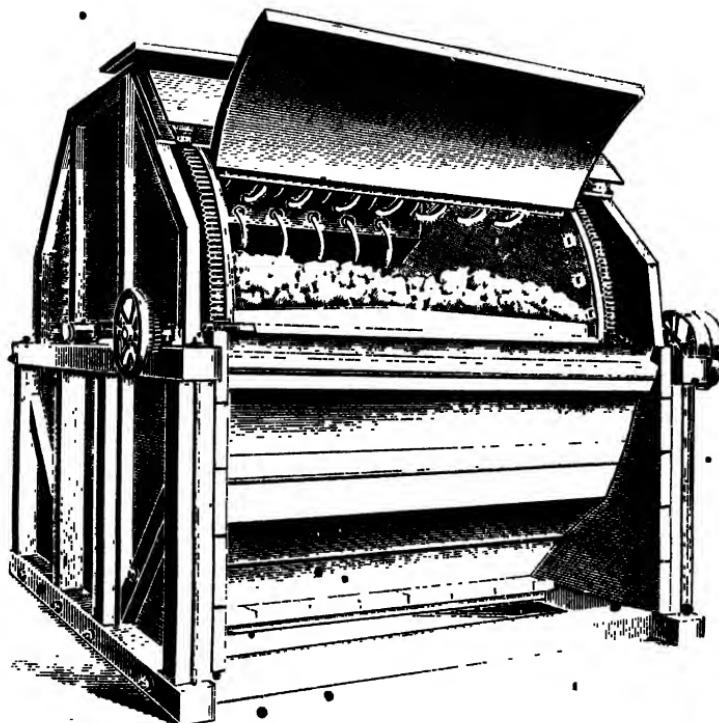


FIG. 13.—Delahunty's dyeing machine.

revolve inside an outer wooden casing. The interior of the revolving drum is fitted with hooks or fingers, whose action is to keep the material open. One segment of the drum is made to open, so that the loose cotton or wool to be dyed can be inserted. By suitable gearing the drum can be revolved;

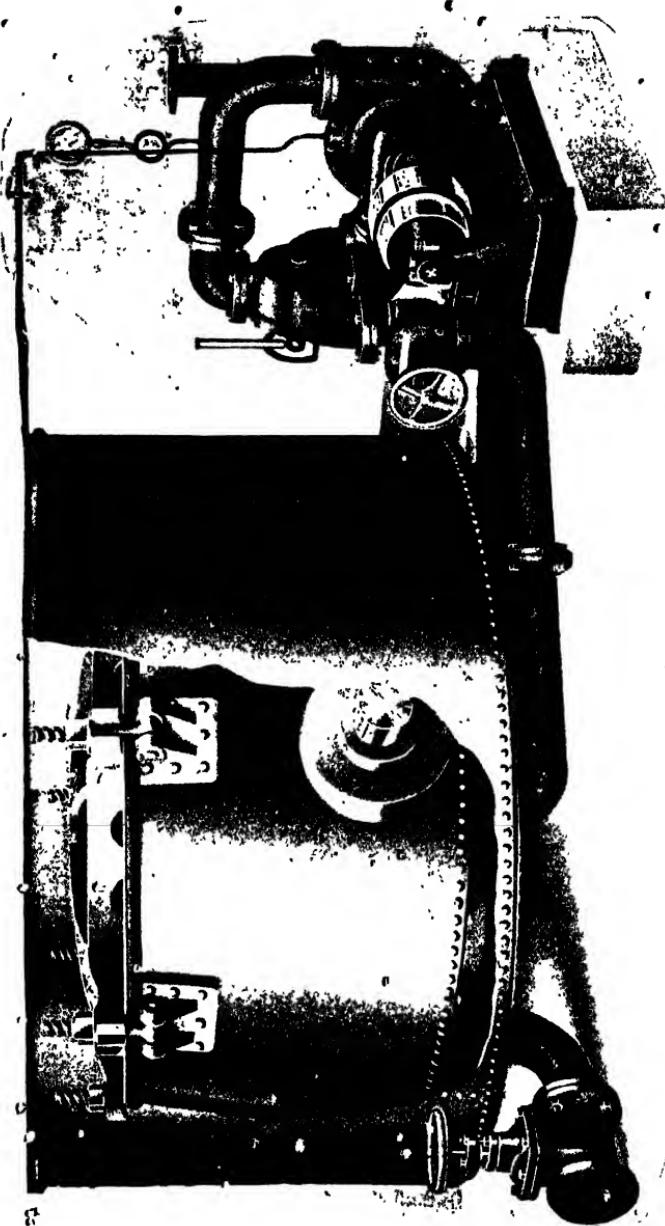


FIG. 14.—Machine for dyeing loose cotton or wool. (The Longclose Engineering Co., Ltd.)

and the dye-liquor, which is in the lower half of the wooden casing, penetrates through the lattice work of the drum, and dyes the material contained in it. The construction of the machine is well shown in the drawing, while the mode of working is obvious from it and the description just given. The machine is very successful, and well adapted for dyeing loose, or raw wool and cotton. The material may be scoured, bleached, dyed, or otherwise treated in this machine. The Obermaier machine, presently to be described, may also be used for dyeing loose cotton or wool.

The Longclose machine for dyeing loose wool and cotton is a very satisfactory piece of apparatus. It is shown in Fig. 14, the dye liquor being forced through the loose wool in a circular container.

*Dyeing Slubbing, Sliver or Carded Cotton and Wool.*—It is found in practice that the dyeing of loose wool or cotton is not altogether satisfactory—the impurities they naturally contain interfere with the purity of the shade they will take. Then, again, the dyes and mordants used in dyeing them are found to have some action on the wire of the carding engine through which they are passed ; at any rate a card does not last as long when working dyed cotton or wool as when used on undyed cotton or wool fibres. Yet for the production of certain fancy yarns for weaving some special classes of fabrics, it is desirable to dye the cotton or wool before it is spun into thread. The best plan is undoubtedly to dye the fibre after it has been carded and partly spun into what is known as slubbing or sliver. All the impurities have been removed, the cotton fibres are laid straight, and so it becomes much easier to dye. On the other hand, as it is necessary to keep the sliver or slubbing straight and level no working about in the dye-liquors can be allowed to take place, and so such must be dyed in specially constructed machines, and one of the best of these is the Obermaier dyeing machine which is

illustrated in Fig. 15. The Obermaier apparatus consists of a dye-vat A. In this is placed a cage consisting of an inner perforated metal cylinder C, and an outer perforated metal cylinder D; between these two is placed the material to be dyed. C is in contact with the suction end of a centrifugal pump P, the delivery end of which discharges into the dye-vat A. The working of the machine is as follows. The slubbing or sliver is placed in the space between C and D rather

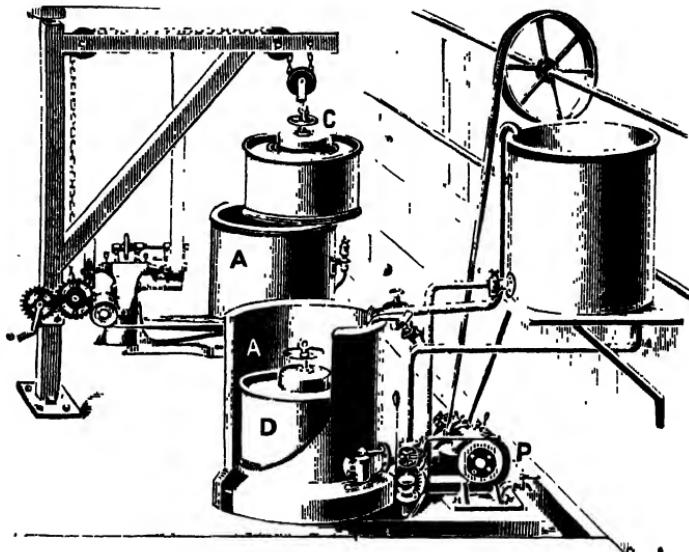


FIG. 15. Obermaier dyeing machine.

tightly so that it will not move about. Then the inner cage is placed in the dye-vat as shown. The vat is filled with the dye-liquor which can be heated up by a steam pipe. The pump is set in motion, the dye-liquor is drawn from A to C, and, in so doing, passes through the material packed in B and dyes it. The circulation of the liquor is carried on as long as experience shows to be necessary. The dye-liquor is run off, hot water is run in to wash the dyed material, and the pump is kept running for some time to ensure

thorough rinsing; then the water is run off, and by keeping the pump running and air going through a certain amount of drying can be effected. This machine works very well, and, with a little experience, constant results can be obtained. The slubbing or sliver may be scoured, bleached, rinsed, dyed, washed, soaped, or otherwise treated without removing it from the machine, which is a most decided advantage.

**Yarn-dyeing Machine.**—In Fig. 16 is given an illustration of a machine for dyeing yarn in the hank form. The illustration gives a very good idea of the machine. It consists of a wooden dye-vat which can be heated by steam pipes in the

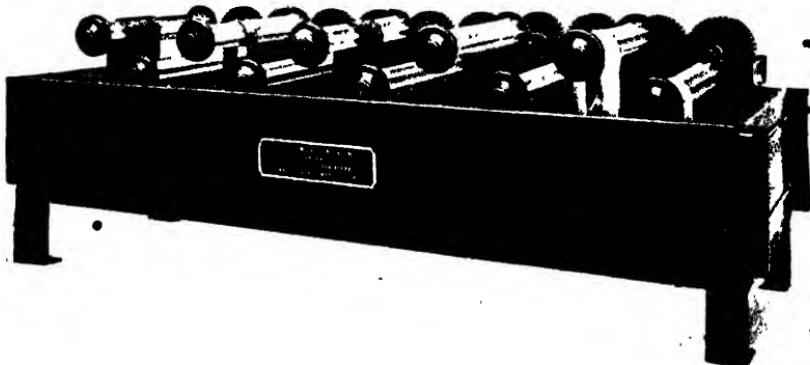


FIG. 16. Hank-dyeing machine. (S. Spence & Sons.)

usual way. Extending over the vat are a number of reels or bobbins; these are made of fluted porcelain; these reels are in connection with suitable gearing so that they can be revolved. There is also a hydraulic arrangement by means of which the reels can be lifted bodily in and out of the dye-vat for the purpose of taking on and off, "doffing," the hanks of yarn for the reels. A reel will hold about two pounds of yarn. The working of the machine is simple. The vat is filled with the requisite dye-liquor. The reels, which are lifted out of the vat, are then charged with the yarn, which has been previously wetted out. They are then

set in revolution and dropped into the dye-vat and kept there until it is seen that the yarn has acquired the desired shade. The reels are lifted out and the hanks removed, when the machine is ready for another lot of yarn. There are several makes of hank-dyeing machines of this type, and as a rule they work very well. The only source of trouble is a slight tendency for the yarn on one reel, if hung loosely, of becoming

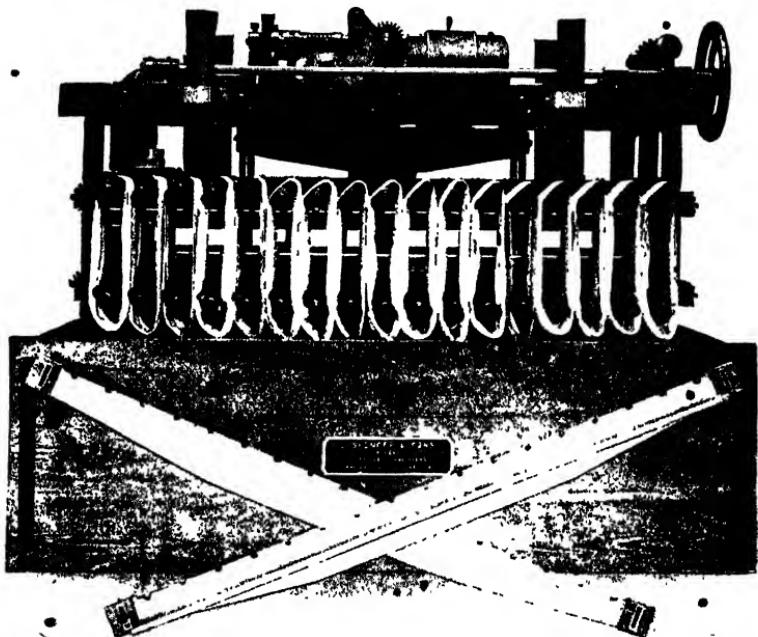


FIG. 16A.—Hank-dyeing machine in charging position. (S. Spencer & Sons.)

entangled with the yarn on one of the other reels. This is to some extent obviated by hanging in the bottom of the hank a roller which acts as a weight and keeps the yarn stretched and so prevents it flying about. To some makes of these machines a hank winder is attached.

Another type of hank-dyeing machine is shown in Fig. 16A.

**Klauder-Weldon Hank-dyeing Machine.**—This is illus-

trated in Fig. 17. This machine consists of a half-cylindrical dye-vat built of wood. On a central axis is built two discs or rod carriers which can revolve in the dye-vat, the revolution being given by suitable gearing, which is shown at the side of the machine. On the outer edge of the discs

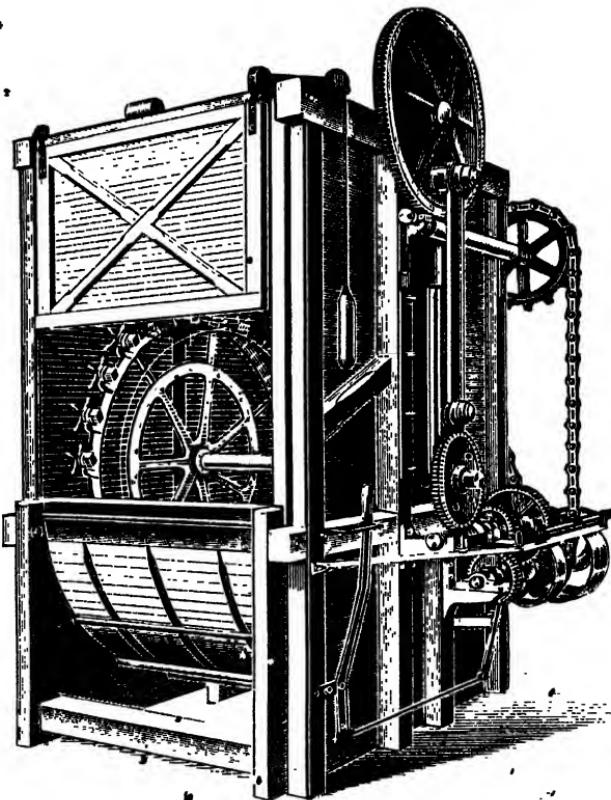


FIG. 17.—Klauder-Weldon dyeing machine.

are clips for carrying rods, on which one end of the hanks of yarn is hung, while the other end is placed on a similar rod carried near the axle. The revolution of the discs carries the yarn through the dye-liquor contained in the lower semi-cylindrical part of the machine previously alluded

to. At a certain point, every revolution of the discs, the rods carrying the yarns are turned a little ; this causes the yarn to move on the rods, and this motion helps to bring about greater evenness of dyeing. The most modern form of this machine is provided with an arrangement by means of which the whole batch of yarn can be lifted out of the dye-liquor. Arrangements are made by which from time to time fresh quantities of dye can be added if required to bring up the dyed yarn to any desired shade. This machine works well and gives good results. Beyond the necessary labour in charging and discharging, and a little attention from time to time, as the operation proceeds, to see if the dyeing is coming up to shade, the machine requires little attention. Many other forms of hank-dyeing machines have been devised : there is Corron's, in which an ordinary rectangular dye-vat is used. Round this is a framework which carries a lifting and falling arrangement that travels to and fro along the vat. The hanks of yarn are hung on rods of a special construction designed to open them out in a manner as nearly approaching handwork as is possible. The machine works in this way : The lifting arrangement is at one end of the vat, the hanks are hung on the rods and placed in the vat. Then the lifter is set in motion and moves along the vat ; as it does so it lifts up each rod full of yarn, turns it over, opening out the yarn in so doing, then it drops it again in the vat. When it has travelled to the end of the vat it returns, picking up the rods of yarn in so doing, and this motion is kept up until the dyeing is completed. This machine is very ingenious. A type of machine which has been made by several makers consists of an ordinary rectangular dye-vat surrounded with a framework carrying a number of sets of endless chains, the links of which carry fingers. The hanks of yarn are hung on rods at one end of which is a tooth wheel that when in position fits into a rack

on the side of the vat. The action of the machine is this : The hanks are hung on the rods and placed at the entrance end of the vat, by the moving of the chains it is carried along the vat and at the same time revolves, thus turning over the yarn which hangs in the dye-liquor ; when it reaches the opposite end of the vat, the rod full of yarn is lifted out, carried upwards and then towards the other end of the vat when it is again dropped into the dye-vat to go through



FIG. 18.—Ceentonip hank-dyeing machine. (S. Spencer & Sons.)

the same cycle of movements, which is continued until the yarn is properly dyed.

Another machine for dyeing and otherwise treating yarn is that made by Spencer & Sons, of Manchester. Its simple, yet efficient, character is shown in Fig. 18.

An improved form of hank-dyeing machine is also being made by the Longelose Engineering Co. Ltd. In this machine, particular care has been paid to ensure perfect circulation of the dye-liquor, so that even and level dyeing may be obtained. This machine is shown in Figs. 19A and 19B.

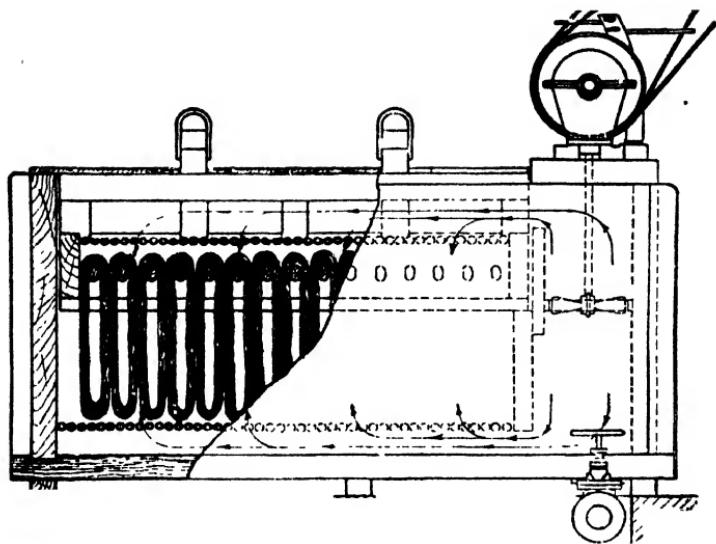


FIG. 19A.—Hank-dyeing machine (longitudinal section). (The Longclose Engineering Co., Ltd.)

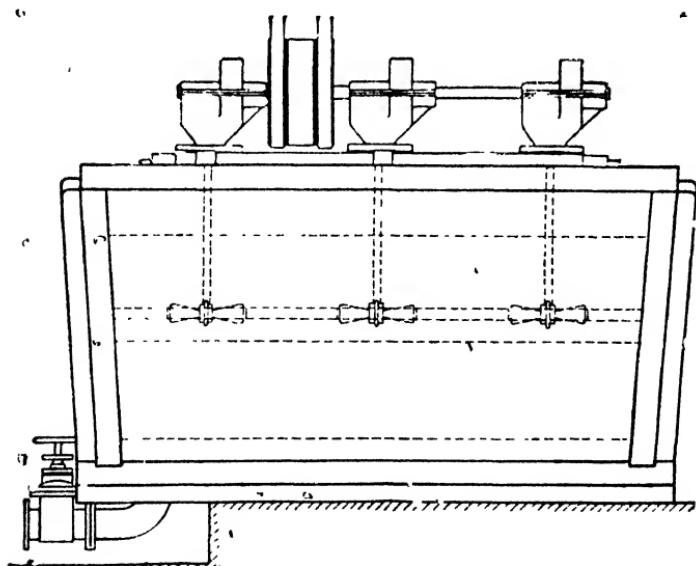


FIG. 19B.—Hank-dyeing machine (cross section). (The Longclose Engineering Co., Ltd.)

*Cop Dyeing.*—In weaving fancy-coloured fabrics the ordinary mode is to dye the yarn in the hank form, then those which have to be used for the weft are wound into the cop form for placing in the shuttles. The cop form is that in which the yarn leaves the spinning frame, and necessarily apart from the dyeing there is labour involved in reeling it into hanks and winding it back again into the cop form; not only so, but there is necessarily some waste made in these operations. Many attempts have been made, with more or less success, to dye the yarn while in the cop form and so save the cost of the hanking and copping above referred to, as well as the waste which occurs. Cops cannot be satisfactorily dyed by simple immersion in a boiling dye-bath; the outside becomes dyed but the central portions as often as not remain quite white, and there is a distinct grading of colour or shade throughout the cop, the outer portions being deeply dyed while the middle portion will only have a medium shade and the central portions either not being dyed at all or only faintly tinted, much depending on the firmness with which the cop has been wound. A soft, loosely wound cop is much more thoroughly dyed than a hard, tightly wound cop. This uneven dyeing of the cops is not satisfactory, and must be avoided if cop dyeing is to be a success. Many dyers have turned their attention to this question of dyeing yarn in the cop form, and many machines have been devised for the purpose; some of these have not been a success, but a few have been found to yield satisfactory results and proved in practice very successful. In all machines for dyeing cops one principle has been adopted—that of drawing or forcing the dye-liquor through the cop.

**Graemiger's Cop-dyeing Machine.**—This is shown in section in Figs. 20A and 20B. Although simple in its work it is somewhat complex in its construction and difficult to describe. The machine consists of a dye-vat to hold the requisite

dye-liquors. In the upper portions of this is an iron casting formed with four chambers, the two lower ones of which are

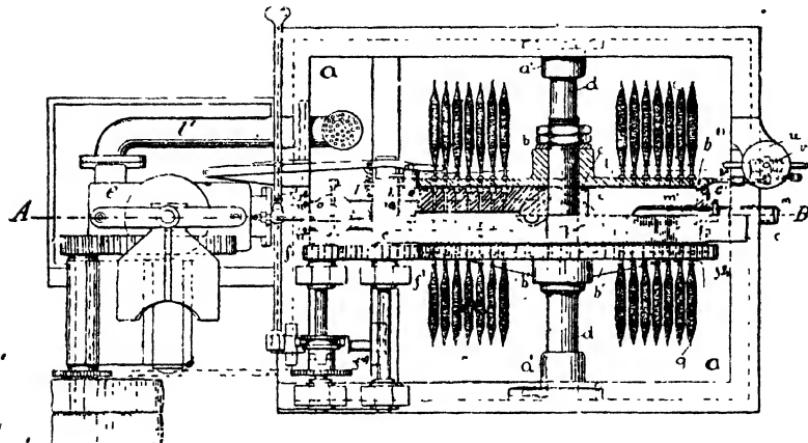


FIG. 20A. —Graemiger cop-dyeing machine.

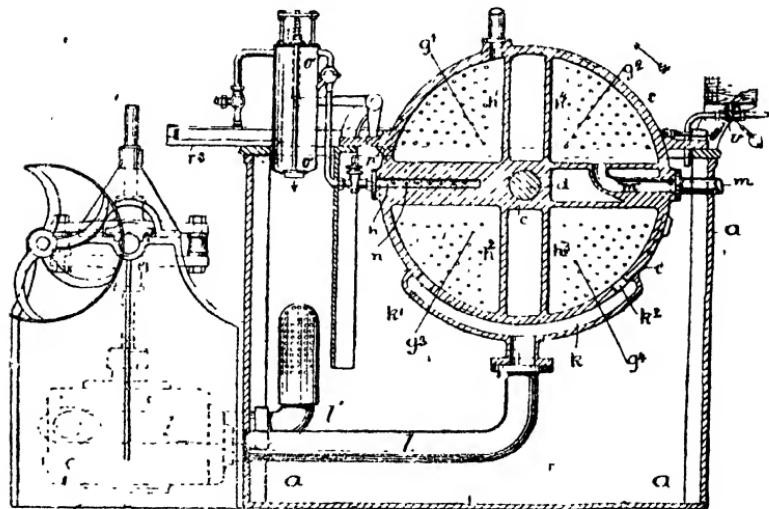


FIG. 20B.—Graemiger cop-dyeing machine.

immersed in the dye-liquor while the upper chambers are above it. The sides of this casting are formed of metal plates

which fit tightly against the casting and form as nearly air- and water-tight joints with it as it is possible to make. These metal plates are on a spindle and can be rotated. They are perforated and made to carry spindles, on which are placed the cops to be dyed. The two lower chambers are in connection with a pump which draws the air from them and so creates a vacuum inside the chambers. To fill this, liquor from the dye-vat passes through the cops and into the chambers, and is in turn drawn through the pump and returned to the dye-vat. In this way there is a continual circulation of dye-liquors from the vat through the cops, chambers and pump back to the vat again. The left upper chamber is practically a blank chamber. Those portions of the cop carriers in contact with it are filled with cops, which are placed on perforated spindles; the discs are given a quarter revolution which brings the cops into the dye-liquor and in connection with the left lower chamber and are dyed. At the same time the section of the cop carriers now in contact with the left top chamber is filled with a new lot of cops, another quarter of a revolution is given to the cop carriers, which immerse the new lot of cops in the dye-liquor. The third quarter of the cop plates is filled with cops. A third movement of the cop plates now takes place; this brings the first lot of cops out of the dye-liquor and in contact with the right upper chamber, where the surplus liquor is drawn out of them and returned to the dye-vat. Another revolution brings the cops back to their first position, they are now removed and a new lot substituted. These proceedings go on continuously. Although not quite free from defects the machine gives very good results, the cops being very uniformly dyed through.

**Beaumont's Cop-dyeing Machine.**—This is illustrated in Fig. 21. It consists of a copper hemispherical dye-vessel which is provided with a tightly fitting lid, although this is

not needed in all cases. The bottom of the vessel is in communication with the suction end of a centrifugal pump, while the delivery end of the pump is attached to the upper end of the dye-vessel, the action of the pump' being to secure a constant circulation of dye-liquor from the bottom to the top of the dye-vessel. Arrangements are provided by a peculiar and ingenious contrivance fitted in one side of the dye-

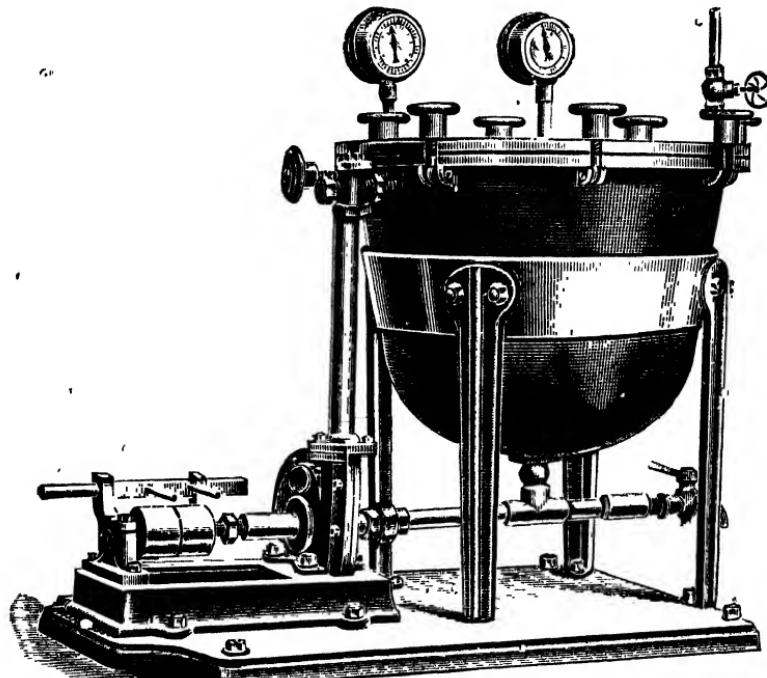


FIG. 21.—Beaumont's cop-dyeing machine.

kettle for introducing steam to heat the dye-liquor to any required degree. As in most forms of cop-dyeing machines, the cops are placed on perforated metal spindles. The cops and spindles are inserted in holes in a perforated metal plate, and over them is placed a thin metal plate, technically called the antifloater, whose object is to prevent the cops from becoming detached from the plate. This plate, full of

cops, is now placed in the dye-vessel and rests upon a flange which is provided for that purpose. When the cop plate is in position the dye-vessel is divided into two chambers—a lower chamber and an upper one, in the latter being the cops.

The pump draws liquor from the chamber under the cop plate and so creates a vacuum, which, during the working of the machine, ranges from 10 to 20 inches in degree. To supply this vacuum, dye-liquor is drawn from the upper chamber through the cops. The pump returns the liquor to the dye-vessel. A very rapid circulation of dye-liquor takes place, from 25 to 50 gallons per minute passing through the cops and pump. From five to ten minutes is sufficient to dye the cops. The machine is simple in its construction and gives good results, the cops being completely dyed through.

- One important consideration in cop dyeing is to be able to dye successive batches of cops to exactly the same shade, and this is quite possible with this machine.

**Young & Crippin's Cop-dyeing Machine.**—So far as simplicity of construction is concerned this lies between the two preceding machines. It consists of four parts with some accessory mechanism. There is first a dye-liquor storage tank at the base of the apparatus in which the liquor is kept stored and boiling (if necessary ready for use), above this and at the front end is the dye-chamber, this communicates at its lower end by a pipe with the dye-liquor in the dye-vat. Then there is a large vacuum chamber, in which by means of an injector a vacuum can be formed, this directly communicates with a liquor-receiving chamber, which again in turn is in communication with the upper part of the dye-chamber. The cops are placed on perforated spindles as usual, and these on a perforated plate, and are kept in place by a plate which is screwed down on them. The charged cop plate is placed in the dye-chamber on which a cover is

placed and screwed down. By means of a lever the injector is set at work, a vacuum created in the vacuum and receiving chambers, the consequence being that dye-liquor is drawn from the vat through the cops in the dye-chamber into the receiving chamber. When a certain quantity of liquor has passed through, by a movement of a lever, the vacuum is destroyed, and the dye-liquor runs back into the dye-vat; these operations are repeated until from past experience of the working of the machine it is thought sufficient has passed through to dye the cops, when the dye-chamber is opened and the cops taken out. This machine works very well.

**Mommer's Cop-dyeing Machine.**—This is in use in several continental dye-works. The central portion of this machine is a rectangular dye-chamber, which can be hermetically closed by hinged doors, the cops are placed side by side on trays provided with perforated bottoms, the trays being placed one on the top of the other in the dye-chamber. From the top of the dye-chamber passes a pipe to a centrifugal pump, and a similar pipe passes from the bottom of the chamber to the pump. A separate vat contains the dye-liquor which is used. The pump forces the dye-liquor through the cops which take up the dye. Arrangements are provided by which the direction of the flow of the dye-liquor can be changed. This machine gives fairly good results, not perhaps equal to those with the machines previously described.

Excellent modern forms of Cop-dyeing machines are shown in Figs. 22 and 23, and which are made by the Longelose Engineering Co. In each of these machines, the textile material is stationary and through it is pumped the dye liquor, under conditions such that maximum penetration is obtained.

**Warp-dyeing Machines.**—Although many warps, especially for fancy fabrics, are prepared from yarns dyed in the

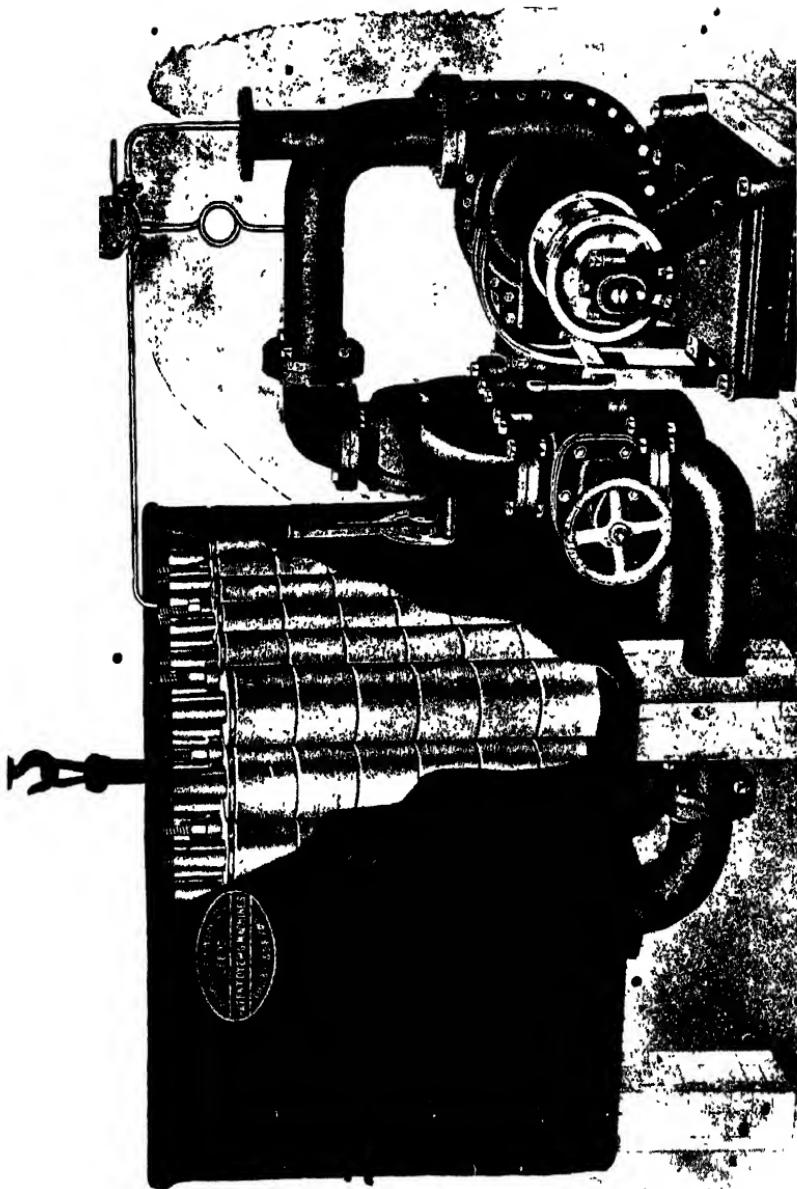


FIG. 22.—Cop-dyeing machine. (The Longclose Engineering Co., Ltd.)

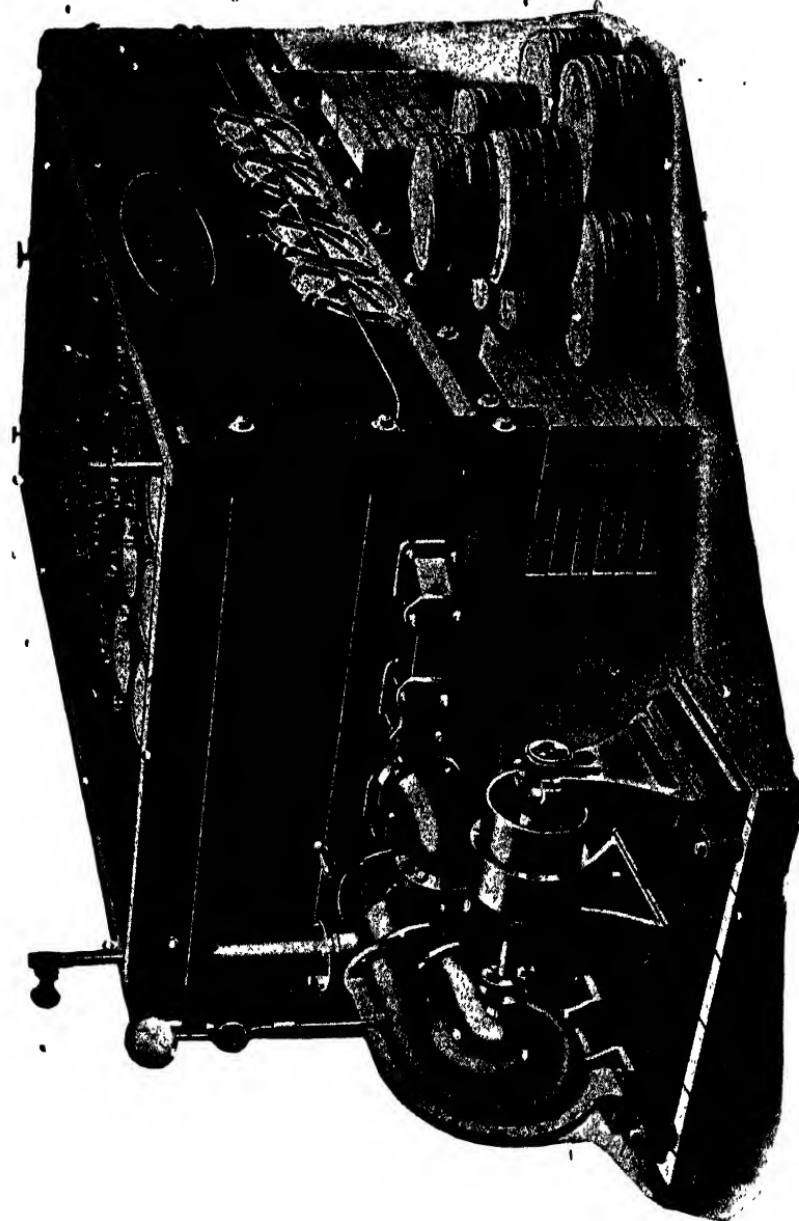


FIG. 23.—Cheese-dyeing machine. (The Longclose Engineering Co., Ltd.)

hank or cop form, yet it is found advantageous when a warp is of one colour, a self-colour as it is called, to form the warp from grey or white yarns and to dye it after warping. If the warp were so wound as to be able to go into an Obermaier dyeing machine, it would be possible to dye it in that machine, but generally warps are dyed in the open form and are passed through a dyeing vat, commonly called a warp-vat, which is constructed as shown in Fig. 24. These warp-dyeing machines generally consist of a long rectangular wooden dye-vat, divided by two partitions into three compartments, each provided with steam pipes to heat up its contents ; between the first and second and between the second and third com-

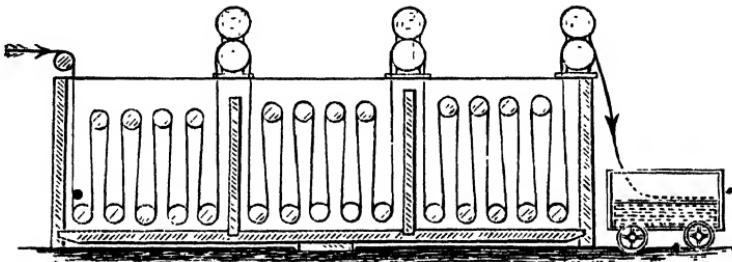


FIG. 24.—Warp-dyeing machine.

partments is fitted a pair of squeezing rollers, while the third compartment is fitted with a heavier pair of squeezing rollers. Motion is given to these rollers by suitable gearing, and they serve to draw the warp through the machine. Guide rollers are fitted in the compartment, and the warp being taken round these, it passes several times up and down and through the dye-liquors contained in the compartments. These warp-dyeing machines may be made of sufficient width to take one, two, three or more warps at one time as desired. The three compartments of the machine may contain different liquids of all the same liquid according as the nature of the shade to be dyed demands. The passage is done slowly so

as to give the warp time to absorb the liquors and take up the dye. When all the length of warp has been sent through, it is said to have been dyed "one end." Sometimes this will be enough, but often it is not, and so the warp is sent through again, given another end, and still again if the full shade has not been attained. After being dyed in this machine the warp is sent through another one containing various wash liquors, to finish the process.

Fig. 25 shows a warp-dyeing machine similar to, but a

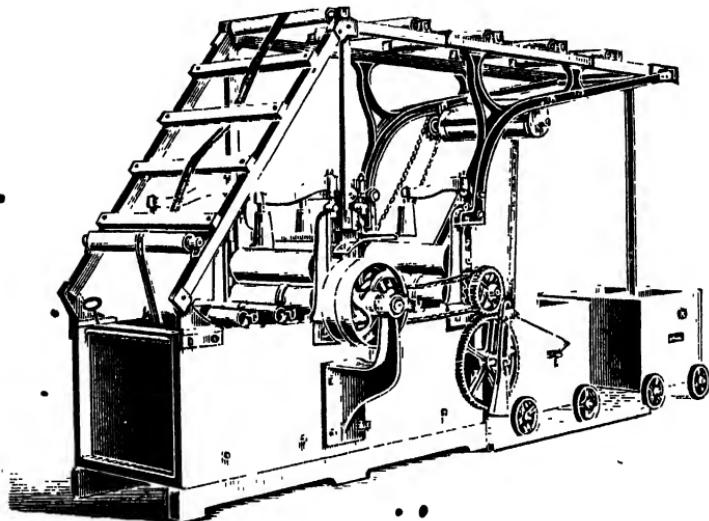


FIG. 25.—Warp-dyeing machine.

little more elaborate in construction than the vats just described.

**Piece-dyeing Machines.**—Wherever it is possible it is far more preferable to dye textile fabrics in the form of woven pieces rather than in the yarn from which they are woven. During the process of weaving it is quite impossible to avoid the material getting dirty and somewhat greasy, and the operations of scouring necessary to remove this dirt and grease has an impairing action on the colour if dyed yarns

have been used in weaving it. This is avoided when the pieces are woven first and dyed afterwards, and this can always be done when the cloths are dyed in one colour only.

Of course when the goods are fancy goods containing several colours they have to be woven from dyed yarns.

The most common form of machine in which pieces are dyed is The Jigger, commonly called the jig. This is shown in Fig. 26. It consists of a dye-vessel made sufficiently long to take the piece full width—wide at the top and narrow at the bottom. At the top at each side is placed a

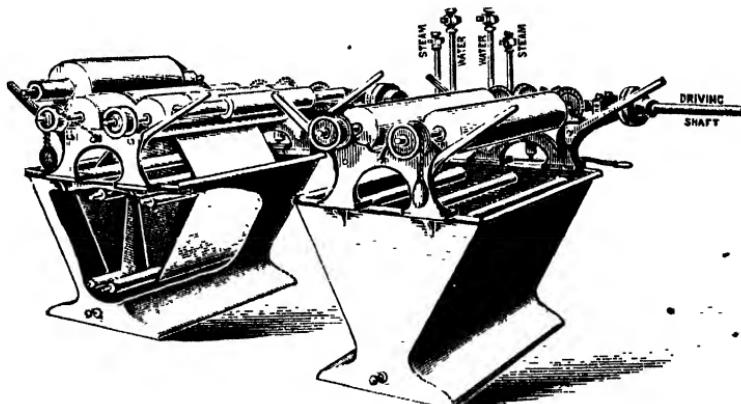


FIG. 26.—Dye-jig. (The Longelose Engineering Co., Ltd.)

large winding roller on which the cloth is wound. At the bottom of the jig is placed a guide roller round which passes the cloth. In working, the cloth is first wound on one of the rollers, then threaded through the guide rollers and attached to the other winding roller. When this is done dye-liquor is run into the jig, the gearing set in motion, and the cloth wound from the full on to the empty roller. With the object of keeping the piece tight, a heavy press'roller is arranged to bear on the cloth on the full roller. When all the cloth has passed from one roller to the other it is said to have

been given "one end." The direction of motion is now changed, and the cloth sent in the opposite direction through the jig, and the piece has now received another "end." This alternation from one roller to the other is continued as long as is deemed necessary, much depending on the depth of colour which is being dyed—some pale shades may only take two or three ends, deeper shades may take more. When dyeing wool with acid colours which are all absorbed from the dye-liquor, or the bath is exhausted, it is a good plan to run the pieces several more ends so as to ensure thorough fixation of the dye on the cloth. It is not advisable in working these jigs to add the whole of the dye to the liquor at the commencement, but only a part of it; then when one end is given, another portion of the dye may be added; such portions being always in the form of solution. Adding dyes in powder form inevitably leads to the production of colour specks on the finished goods. The reason for thus adding the dyestuff in portions is that with some dyes the affinity for the fibre is so great that if all were added at once it would all be absorbed before the cloth had been given one end; and, further, the cloth would be very deep at the front end, while it would shade off to no colour at the other end. By adding the dye in portions this difficulty is overcome and more level shades are obtained; it is met with in all cases of jigger dyeing, but it is most common in dyeing cotton or wool with basic dyes like magenta, auramine, methyl violet or brilliant green, and in dyeing wool with acid dyes like acid green, formyl violets, azo scarlet, or acid yellow. Recently a jigger, automatic in its reversing action and also in respect of the period of its action, has been placed on the market, and appears likely to be in demand.

**The Jig Wince or Wince Dye Beck.** - This dyeing machine is very largely used, particularly in the dyeing of woollen cloths. It is made by many makers, and varies somewhat

in form accordingly. Figs. 27, 28, and 29 show three forms by different makers. In any make the jig wince, or wince dye beck, consists of a large rectangular, or, in some cases, hemicylindrical dye-vat. Probably the best shape would be to have a vat with one straight side at the front, and one

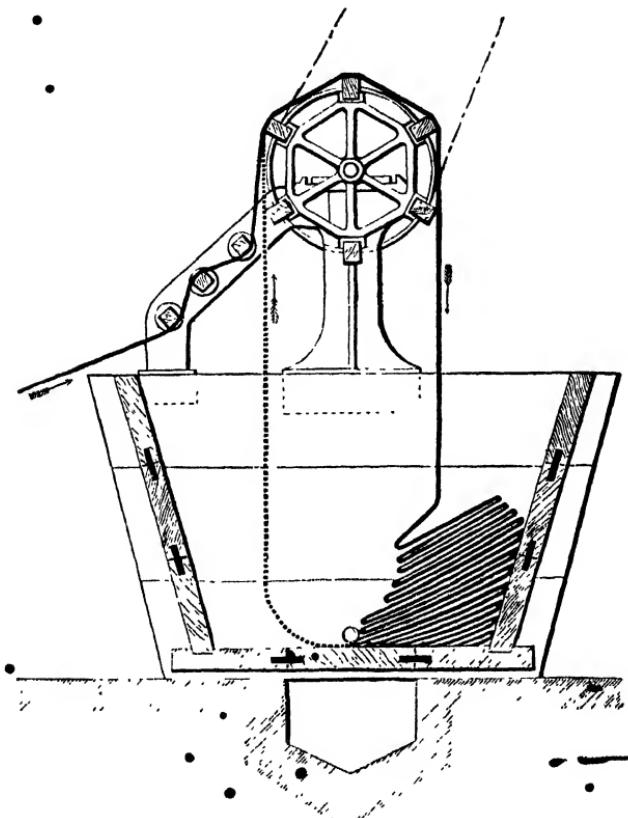


FIG. 27.—Jig wince.

curved side at the back. In some a small guide roller is fitted at the bottom, under which the pieces to be dyed pass. Steam pipes are provided for heating the dye-liquors. The becks should be fitted with a false bottom made of wood, perforated with holes, or of wooden lattice work, and below

which the steam pipes are placed ; the object being to prevent the pieces from coming in contact with the steam pipe, and so preventing the production of stains. Above the dye-vat, and towards the back, is the wince, a revolving skeleton wheel, which draws the pieces out of the dye-vat at the front, and delivers them into it again at the back. The construction of this wince is well shown in the drawings. The wince

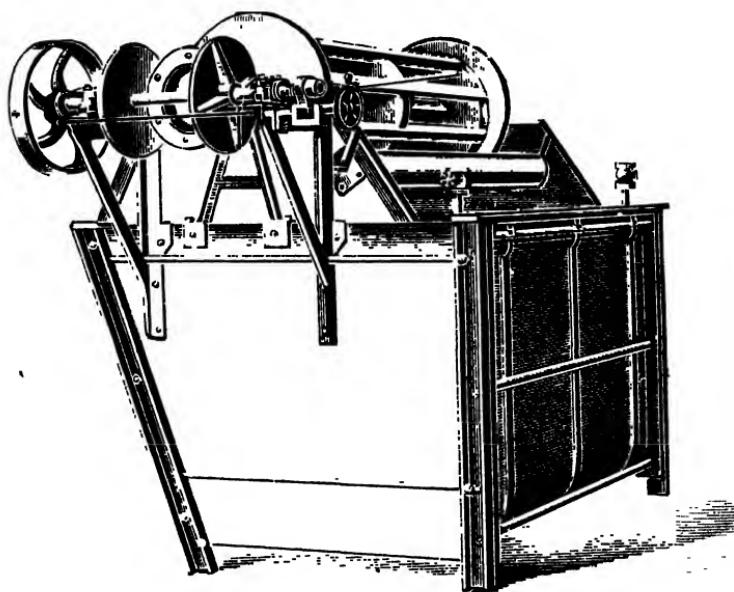


FIG. 28. -Cloth-dyeing machine.

will take the pieces full breadth, but often they are somewhat folded, and so several pieces, four, five, or six strings as they are called, can be dealt with at one time. In this case a guide rail is provided in the front part of the machine. In this rail are pegs which serve to keep the pieces of cloth separate, and so prevent entanglements. The pieces are stitched end to end so as to form an endless band. When running through the vat they fall down in folds at the back part of the beck,

and are drawn out of the bottom and up in the front. Each part thus remains for some time in the dye-liquor, during which it necessarily takes up the dye.

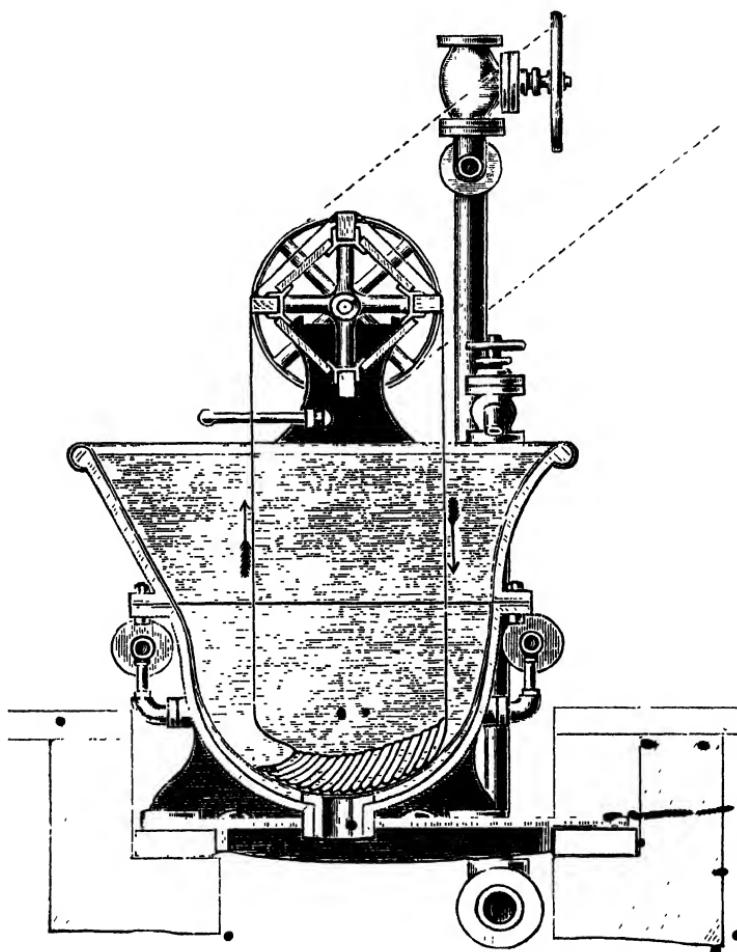


FIG. 29.—Dye beck.

Other wince-dyeing machines suitable for knitted fabrics made by the Longclose Engineering Co. Ltd. are shown in Fig. 30.

In the jig and wince-dyeing machines the pieces necessarily are for a part of the time—longer in the case of the jigger than in that of the wince—out of the dye-liquor and exposed to the air. In the case of some dyes, indigo especially, this is not desirable, and yet it is advisable to run the cloth open for some time in the liquor, so as to get it thoroughly impregnated with the dye-liquor, or to become dyed. This may be done on such a machine as is shown

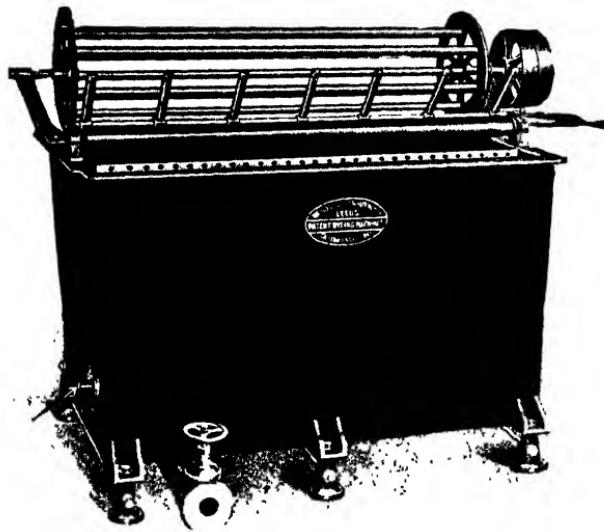


Fig. 30.—Machine for dyeing knitted fabrics. (The Longclose Engineering Co., Ltd.)

in Fig. 32, but having all the guide rollers below the liquor, so that at no time is the piece out of the liquor, except, of course, when entering and leaving. The so-called hawking machines have also this object in view, and Fig. 31 is an illustration of a hawking machine. There is the dye-vat as usual ; in this is suspended the drawing mechanism, whose construction is well shown in the drawing. This is a pair of rollers driven by suitable gearing, between which the cloth

passes, and by which it is drawn through the machine. A small roller ensures the cloth properly leaving the large

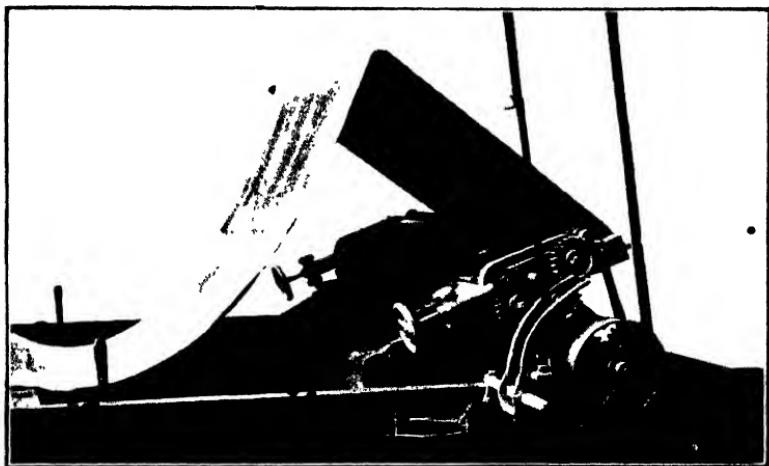


FIG. 31.—Machine for hawking cloth.

rollers; then there is a lattice-work arrangement over which the pieces are drawn. In actual work the whole of this ar-

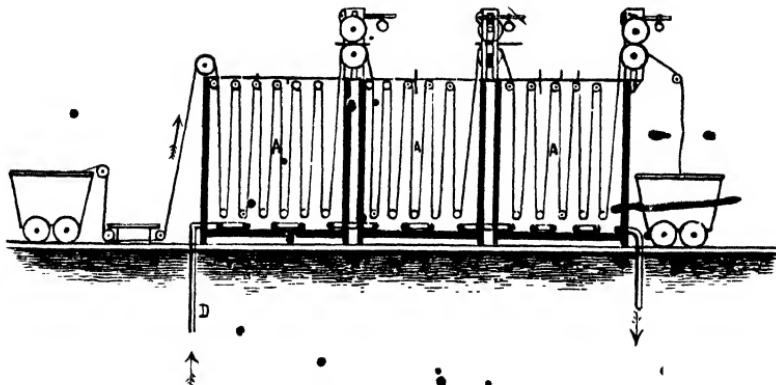


FIG. 32.—Continuous dyeing machine.

angement is below the surface of the dye-liquor in the vat. The piece to be dyed is threaded through the machine, the

ends stitched together. Then the arrangement is lowered into the dye-vat and set into motion, whereby the cloth is drawn continuously in the open form through the dye-liquor, this being done as long as experience shows to be necessary. This hawking machine will be found useful in dyeing indigo on cotton or wool, or in dyeing cotton cloths

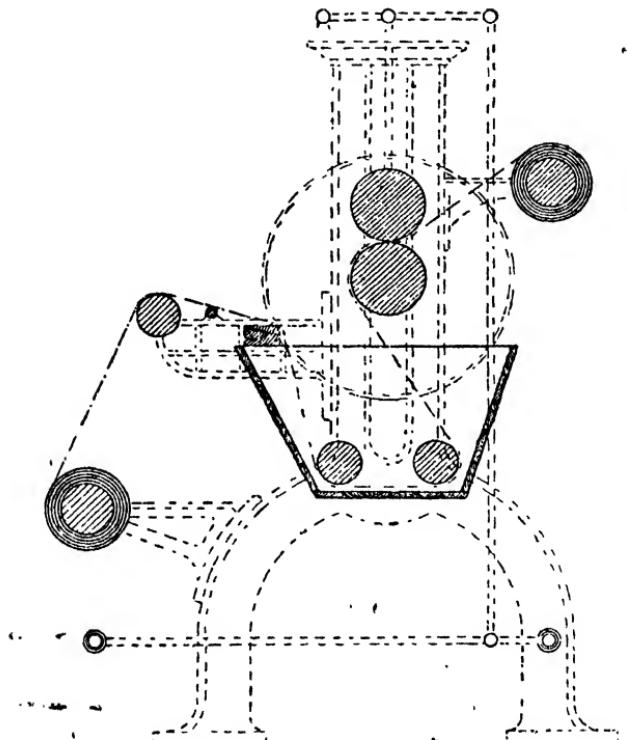


FIG. 33.—Padding machine.

with such dyes as Sulphur blacks, where it is necessary to keep the goods below the surface of the dye-liquor during the operation.

Fig. 32 shows a form of cloth-dyeing machine much used in the cotton trade. It consists of a number of compartments fitted with guide rollers at top and bottom, and round which

the cloth is threaded, so that it passes up and down in the dye-liquor several times. Between each two compartments is a pair of squeezing rollers to press out all surplus liquors. All the compartments may be filled with the same dye-liquor, or with different dye-liquors and developing liquors, as may

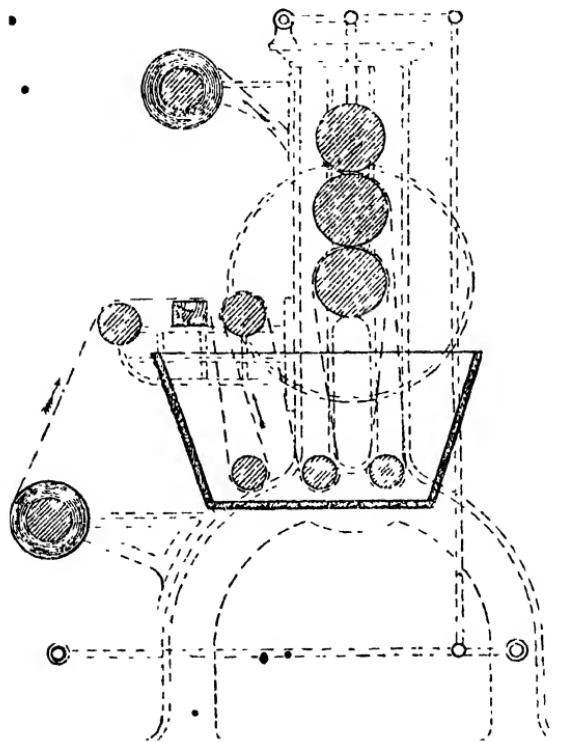


FIG. 34.—Padding machine.

be most convenient and required for the work in hand. Such a machine is used in dyeing logwood black, aniline black, and many of the direct colours, etc. From the direct colours a large number of light shades are dyed on to cotton cloth by the process known as padding ; this consists in passing the cloth through a liquor containing the dye-stuff, usually a

little phosphate of soda is added, then between squeezing rollers, and finally drying the cloth.

**Padding Machine.**—For this process there is used what is called a padding machine. This is shown in Figs. 33 and 34. It consists essentially of a trough, which contains two or more guide rollers, and in this is placed the padding liquor. Above the trough is fitted squeezing rollers, sometimes two as in Fig. 33, or three as in Fig. 34. Besides these, there are winding and beaming and other guide rollers. Fig. 33 shows the simplest padding machine, where the cloth passes once through the liquor and through the squeezing rollers. In Fig. 34 the cloth passes several times through the liquor and twice through the squeezing rollers, thus ensuring a more perfect impregnation of the cloth with the dye-liquor, and therefore a more uniform dyeing of the cloth.

## CHAPTER IV.

### THE PRINCIPLES AND PRACTICE OF COTTON DYEING.

*Different Methods of Dyeing Cotton Yarn and Fabrics.*—Students of cotton dyeing should have a good knowledge of the principles that underlie the processes of dyeing cotton fabrics. It is only by recognising these principles and then endeavouring to apply them to each individual case of dyeing, that the dyer or student will obtain a thorough grasp of his subject. It is the aim of the author to lay down these principles in a clear and intelligible form. Cotton is dyed in its loose raw condition, as yarn in the form of hanks, yarn in the form of cops, and in the woven pieces of every kind. Formerly the idea was prevalent among cotton dyers that the process which succeeds with piece goods would not answer with yarns. It is now recognised, however, that this is not so, that a process which will dye cotton yarn will also dye cotton piece goods or loose cotton. The differences which do exist in the practical working of the processes entirely arise from the difference in the form in which the cotton is presented to the dyer, for it must be obvious to any one that the mode of handling a piece of cotton cloth during the time it is in the dye-bath must be different from that of a hank of yarn, a parcel of loose cotton or a number of cops. The various machines used for dyeing all these forms and the manner of working them have been already described.

*Classification of Processes of Dyeing with both Natural and Artificial Dye-Stuffs.*—The dyes, whether natural (derived from the various dyewoods, etc.) or artificial (usually

prepared from coal tar) may according to their varied chemical composition and constitution be divided into several distinct groups. It is not intended here to give any account of them.<sup>1</sup> From the manner in which the various dyes are applied to cotton, linen, wool and other fibres we can divide them into five groups, thus : Group (1) Direct dyes ; (2) Basic dyes ; (3) Acid dyes ; (4) Mordant dyes ; (5) Vat dyes ; (6) Sulphur dyes ; (7) Miscellaneous.

*Group I : Direct Dyes.*—These dyes are now very numerous : they dye cotton, linen and other vegetable fibres from a plain bath, and do not require those fibres to be prepared in any way. Hence the reason of their being named direct, or by some the substantive colours. They will also dye wool and silk. *Group II : Basic Dyes.*—The second group (basic dyes) comprise some of the oldest of the coal-tar dyes ; they dye wool and silk direct from plain baths, but require cotton, linen and other vegetable fibres to be previously prepared in baths of tannic acid, sumach or other tanning material. *Group III : Acid Dyes.*—The third group (acid dyes) are very numerous, and from both their chemical composition and mode of dyeing can be divided into several sub-groups. Their principal feature is that they dye wool and silk from baths containing Glauber's salt and some acid, hence their name of "acid dyes." They do not dye cotton or linen well, some not at all, others are absorbed to a slight extent by the cotton, but only pale tints are produced, while others may be used along with metallic mordants to dye bright but pale and fugitive shades. The acid dyes comprise such as Acid green, Formyl violet, Acid magenta, Azo scarlet, Orange, Thiocarmine R., Patent blues, Wool greens, Indigo extract, Eosines, etc. *Group IV : Mordant Dyes.*—The fourth group (mordant dyes) includes the

<sup>1</sup> Georgievics, "The Chemistry of Dye Stuffs" (Scott, Green & Son), where the composition and properties of the dyes are fully described.

alizarine series of coal-tar colours, logwood, Brazil wood and most natural colours, and some others. The principal feature of these dyes is that they require the cotton to be prepared with some metallic oxide, like those of chrome, alumina and iron before dyeing, and the colour which is got depends partly upon the particular dyestuff used and partly upon the oxide with which the cotton has been prepared.

*Group V : Vat Dyes.*—Among these dyestuffs are to be found some of the fastest colouring matters known, though unfortunately they are generally the most expensive. Vat dyestuffs are usually divided into two main classes, those prepared from authraquinone and those related to Indigo, though the principles underlying the use of both are similar.

A vat dyestuff is capable of existing in two forms, a fully oxidised form completely insoluble in water and a reduced form soluble in alkaline solutions from which they may be dyed on cotton. The reduced or leuco form of a vat dyestuff has an affinity for cotton but the oxidised form has not. Exposure to air of cotton dyed with a leuco-vat dyestuff results in the full development of colour owing to the oxidation of the dyestuff to its insoluble form. As will be seen later, dyeing by means of vat dyestuffs is dependent on these characteristic properties.

Generally shades obtained by means of vat dyes are very fast to light, washing, alkalis, acids, chlorine and most reagents.

*Group VI : Sulphur Dyes.*—These dyestuffs closely resemble the vat dyes in their chemical properties, though quite different in chemical structure. Most sulphur dyestuffs are manufactured by fusing various amino benzene compounds with sodium sulphide. The dyes can exist in oxidised and reduced forms and are applied to cotton while in a reduced condition. Almost without exception, dyeing

with sulphur dyes is carried out by use of the dyestuff dissolved in an aqueous solution of sodium sulphide.

Shades obtained with sulphur dyestuffs are usually very fast to washing and alkalis. They are not much affected by weak acids but more so by strong acids. When treated with chlorine, sulphur dyestuffs are destroyed. Hence sulphur colours as distinguished from most vat dyes are not fast to bleaching.

The various methods for dyeing cotton are, therefore : (1) Direct dyeing ; (2) Direct dyeing followed by fixation with metallic salts ; (3) Direct dyeing followed by fixation with developers ; (4) Direct dyeing followed by fixation with couplers ; (5) Dyeing on tannic or similar mordant ; (6) Dyeing on metallic mordant ; (7) Developing the colour direct on fibre ; (8) Dyeing by impregnating the cotton with the reduced dyestuff, followed by oxidation or steaming. It is, of course, not easy to elaborate a simple scheme of grouping the processes that shall definitely include all processes, but the above grouping will be found as successful as any, and each will be considered as fully as is deemed necessary.

Furthermore, it generally happens that the shades desired in large scale dyeing are not self shades, but can only be obtained by the use of mixtures of dyestuffs. Consequently it is here useful to consider briefly the principles on which colour mixing depends.

It is generally recognised that any colour can be matched by mixing suitable proportions of the three *primary* colours : red, yellow, and blue. The primary colours are characterised by the fact that they cannot be produced by mixture of any other colours.

When primary colours are mixed two at a time, *secondary* colours are produced and of these there are three : orange, green, and purple. By a mixture of primary colours three at a time (one being in excess), or by mixing one primary

with a suitable secondary colour, or by a mixture of two secondary colours, brown, grey, and olive shades are produced, and these are known as *tertiary* colours.

Generally it is recognised that the primary colours are brightest while the tertiary colours are subdued and dull. This is because mixture of the three primaries, red, orange, and blue, in suitable proportions yields black, so that all tertiary colours may, therefore, be considered as containing a certain proportion of black.

All these facts are expressed in the following table :—

Primary Colours.		
Red	Yellow	Blue
Secondary Colours.		
Orange red and yellow	Green yellow and blue	Purple red and blue
Tertiary Colours.		
Brown orange + purple red + yellow      red + blue red + yellow + blue in excess	Olive orange + green red + yellow      yellow + blue red + yellow + blue in excess	Grey green + purple yellow + blue      red + blue red + yellow + blue in excess

## I. DIRECT DYEING.

*Methods of Working with Direct Dyes—Assistants and Aids in Direct Dyeing.*—Nothing in the history of cotton dyeing caused such a revolution in the methods of working as did the introduction, some forty years ago, of the fore-runners (Congo red, Benzo purpurine, Chrysamine, Azo blue) of the now numerous group of direct dyes, followed as they were by the Benzo, Congo, Diamine, Titan, Chicago and Zambesi members of the group. Prior to their introduction cotton dyeing was always more or less complicated and

mordanting methods had to be employed. With the introduction of the direct dyes cotton dyeing has become even more simple than wool or silk dyeing, and now all that is necessary is to prepare a dye-liquor containing the necessary amount of dyestuff and Glauber's salt, or common salt or soda, or some similar body, or a combination thereof. The method of working is to place the cotton in a luke-warm or even in a hot bath, raise to the boil, allow the goods to remain in the boiling bath for half an hour to an hour, then take them out, wring, wash, and dry. This method is simple and will answer for all the dyes of this group. There are some that do not require the working to be done boiling; it is simply necessary to enter the cotton into a boiling bath and work without steam until the bath has cooled down. Furious boiling is not needed—a gentle simmer gives the best results. Uneven dyeing is not characteristic of this group of dyes, unless the cotton is dirty; no matter how the operations are carried on, level dyeing is the rule, not the exception. An enormous variety of shades and tints can be obtained from these dyes, and they can be combined together in every conceivable manner and proportions. No satisfactory explanation has yet been given as to what feature in the chemical composition of these dyestuffs give them such an affinity for the cotton fibre as to enable them to dye in so simple a manner such fast shades as ~~they do~~. It is a fact there is such an affinity and there the matter must rest. It has been found in practice that the efficiency of the dyeing operation depends, primarily, of course, on the particular dye-stuff used, but also upon other factors, that a certain assistant be used. Some dyes work on the cotton better from a bath containing Glauber's salt, while with others common salt works best, while a little soda along with the salt facilitates the dyeing in some cases. It is practically impossible to specify here the best assistant for all

the direct colours, on account of the great number of such dyes which are known, but in the practical recipes given below much useful advice will be found. Then the quantity of such assistants used is of much importance ; there is one proportion at which the best results are obtained for each dye. The dyer should find out for himself by experiment and the use of the dyes he employs in his work what assistant and how much is best, and make his baths up to that strength. With some dyes 10 per cent. of the assistant will be found sufficient, while with others, 25 to 30 per cent. will not be too much. The percentage refers to the weight of the cotton that is taken. One function of the assistants must be pointed out here : it is that in some cases they—especially the alkaline ones, soda, potash, borax, phosphate of soda—help the dyeing by promoting the solubility of the dyestuff in the bath, thereby retarding the exhaustion of the bath and ensuring the production of level shades. The following formulæ show the application of the foregoing principles to the dyeing of numerous shades on to cotton and also the dyes which are applicable, some of the combinations which are possible with these direct dyes, and give some idea of the tints and shades of the colours that can be got by their means. The best assistants to use are also indicated in the formulæ. All the formulæ here given and all that will be given in future chapters are intended for 100 lb. weight of cotton fabrics in any condition, whether of loose cotton, yarn in cops, hanks or warps and woven fabrics of every kind.

#### *1•Direct Dyeing—Reds, etc.*

- (1) *Bright Red.*—Dye with 3 lb. Benzo purpurine 4 B, 3 lb. soda and 15 lb. Glauber's salt. This dye may also be

<sup>1</sup> Equivalent dyestuffs, chemical constitution, reactions, and other information relating to the dyestuffs mentioned in the following formulæ will be found in *The Colour Index* (published by the Society of Dyers and Colourists).

used with 3 lb. soap and 10 lb. soda in the bath with equally good results. (2) *Pale Salmon*.—Prepare a dye-bath with 3 lb. salt, 5 lb. phosphate of soda, 1 lb. soap,  $\frac{1}{2}$  oz. Benzo orange R. For a pale shade like this it is not necessary to heat to the boil, a temperature of 170° to 180° F. is sufficient. (3) *Dark Plum*.—Prepare a dye-bath with 20 lb. of Glauber's salt,  $2\frac{1}{2}$  lb. soap,  $1\frac{1}{2}$  lb. Diamine black RO and 2 lb. Diamine red N. Enter at 180° F., work for a few minutes, then raise to boil and dye to shade; lift, wash, and dry. (4) *Turkey Red*.—Prepare a dye-bath with  $1\frac{1}{2}$  lb. Benzo purpurine 4 B, 1 lb. Brilliant purpurine, 2 lb. soap, 10 lb. borax. Enter the cotton at the boil and work for one hour; lift, wash, and dry. (5) *Lilac Red*.—Prepare the dye-bath with 2 lb. soap, 5 lb. soda, 3 lb. Rose azurine G. Work at the boil for one hour. (6) *Pink*.—Prepare a bath containing 10 lb. soda, 1 oz. Rose azurine B. Enter at a boil and work for one hour, boiling to shade; lift, wash, and dry. (7) *Bordeaux*.—Prepare a dye-bath with 15 lb. Glauber's salt, 5 lb. soda crystals, 3 lb. Diamine fast red F, 1 lb. Diamine violet N, 1 lb. Rose azurine G. Enter cold, then raise to the boil, and work for one and a half hours; lift, wash, and dry. (8) *Rose Pink*.—The dye-bath is made with 2 lb. Erika B, 20 lb. Glauber's salt and 3 lb. soap, working at near the boil to shade. (9) *Brilliant Red*.—Make the dye-bath with  $2\frac{1}{2}$  lb. Brilliant purpurine R. and 25 lb. Glauber's salt, working at the boil for one hour. (10) *Deep Pink*.—Make the dye-bath with  $\frac{1}{2}$  lb. Diamine rose BD,  $\frac{1}{2}$  lb. soda, 1 lb. soap and 5 lb. Glauber's salt, working at 150° F. for half an hour. (11) *Dark Red*.—Use in the dye-bath 3 lb. Diamine red 5 B, 2 lb. soda and 20 lb. Glauber's salt, working at the boil for one hour. (12) *Pink*.—Prepare the dye-bath with 4 oz. Diamine rose BD, 1 lb. Turkey-red oil, 40 lb. Glauber's salt. Dye at the boil for one hour. (13) *Scarlet*.—Prepare the dye-bath with 4 lb. Diamine scarlet 3 B, 1 lb. Turkey-red oil, 20 lb. Glauber's salt. Dye at

the boil for one hour. (14) *Scarlet*.—Prepare the dye-bath with 3 lb. Titan scarlet C,  $\frac{1}{2}$  lb. Titan orange, 50 lb. salt. Work at the boil for thirty minutes, then lift, wash, and dry. The dye-bath is not exhausted and may be used for further lots. (15) *Crimson Red*.—Prepare the dye-bath with 5 lb. Titan scarlet D and 50 lb. salt. Work at the boil for fifty minutes, then lift, wash and dry. The bath is not exhausted, the cotton taking up only about 3 lb. of the dye-stuff ; it may therefore be kept for further use, when for each succeeding lot 3 to  $3\frac{1}{2}$  lb. of colour and 25 lb. of salt only need be added. (16) *Scarlet*.—Prepare the dye-bath with 5 lb. Rosophenine 5 B, dissolved in 50 gallons hot water, 2 gallons caustic soda lye ( $60^{\circ}$  Tw.). When thoroughly dissolved add 150 lb. salt. Make up the bath to 100 gallons. Enter the yarn and work for a quarter to half an hour at about  $180^{\circ}$  F. ; squeeze off, and wash thoroughly in cold water until the water runs off clean. (17) *Rose Red*.—Use 1 lb. Diamine red 10 B, 3 lb. soda and 20 lb. Glauber's salt. (18) *Deep Crimson*.—Use 3 lb. Diamine red 10 B, 3 lb. soda and 20 lb. Glauber's salt. (19) *Claret*.—Use 3 lb. Diamine Bordeaux B, 3 lb. soda and 20 lb. Glauber's salt. (20) *Pink*.—The dye-bath is made with 5 oz. Dianil red 4 B, 5 lb. salt and 3 lb. soda. (21) *Scarlet*.—Use in the dye-bath 3 lb. Dianil red 4 B, 15 lb. salt and 5 lb. soda. Work at the boil for one hour. (22) *Claret*.—Dye with  $1\frac{1}{2}$  lb. Dianil claret G, 3 lb. soda and 20 lb. salt. Work at the boil for one hour. (23) *Maroon*.—Dye with 3 lb. Dianil claret B, 3 lb. soda and 20 lb. salt. Work at the boil for one hour. (24) *Bright Scarlet*.—Use in the dye-bath  $2\frac{1}{2}$  lb. Dianil red 4 B, 5 oz. Dianil orange G, 3 lb. soda and 15 lb. salt. (25) *Dark Maroon*.—Make the dye-bath with 1 lb. Dianil red 4 B, 2 lb. Dianil claret G, 13 oz. Dianil claret B, 5 lb. soda and 20 lb. salt. (26) *Crimson*.—Dye with 3 lb. Congo rubine, 5 lb. soda and 20 lb. Glauber's salt. (27) *Dark Maroon*.—Use in the dye-bath

1 lb. Benzo purpurine 4 B, 3 lb. Congo Corinth G, 3 lb. soda and 20 lb. Glauber's salt, working at the boil to shade. (28) *Pale Fawn Red.*—Use in the dye-bath 1½ oz. Diamine red 5 B, 1½ oz. Diamine catechine G, 3 lb. soda and 10 lb. Glauber's salt. (29) *Rose Red.*—Prepare the dye-bath with ¾ lb. Diamine Bordeaux B, 3 oz. Diamine orange B, 3 lb. soda and 20 lb. salt. (30) *Crimson.*—Use in the dye-bath ¾ lb. Diamine Bordeaux B, 3 oz. Diamine fast yellow B, 3 lb. soda and 20 lb. Glauber's salt. (31) *Salmon.*—Dye with 1½ oz. Diamine fast red F, 1½ oz. Diamine fast yellow B, 3 lb. soda and 10 lb. Glauber's salt. (32) *Terra-Cotta Red.*—Dye with 1½ lb. Diamine brown M, ¾ lb. Diamine fast red F, 3 lb. soda and 20 lb. Glauber's salt. (33) *Lilac Red.*—Dye with 4 lb. Heliotrope BB, 3 lb. soda and 15 lb. Glauber's salt. (34) *Bright Pink.*—Use in the dye-bath 2 oz. Rose azurine G, 1 lb. soda and 10 lb. Glauber's salt. Nearly all the direct reds give good pink tints when used in proportion, varying from 0·1 to 0·25 per cent. of dye-stuff.

#### *Direct Dyeing—Yellows, etc.*

- (1) *Bright Straw.*—Dye in a bath made of ½ lb. Titan yellow GG, 10 lb. salt, for three-quarters of an hour, then lift, wash and dry. (2) *Yellow.*—Prepare a dye-bath with 1 lb. Titan yellow Y, 10 lb. salt. Heat to 180° F., enter the goods, raise to boil, and dye for one hour; lift, wash and dry. (3) *Yellow.*—Prepare the dye-bath with ¼ lb. Diamine fast yellow A, 1 lb. Turkey-red oil, 20 lb. Glauber's salt. Dye at the boil for one hour. (4) *Sun Yellow.*—Prepare the dye-bath with 2 lb. Sun yellow, 30 lb. common salt. Dye at the boil. The bath is kept for further lots. (5) *Yellow.*—Prepare the dye-bath with 1 lb. Direct yellow R, 20 lb. Glauber's salt. Dye at the boil for one hour. (6) *Yellow.*—Prepare the dye-bath with 2 lb. Curcuphenine, 20 lb. common salt. Work

at the boil for one hour; lift, rinse and dry. (7) *Old Gold*.—

Make the dye-bath with 5 lb. Diamine yellow N powder, 20 lb. phosphate of soda, 10 lb. soap. Work at the boil for one hour; finish in the usual way. The bath may be kept for other lots of goods. (8) *Dark Yellow*.—The bath is made from 2 lb. Toluylene orange G, 10 lb. phosphate of soda and 2½ lb. soap, working at the boil to shade.

(9) *Bright Yellow*.—Use 1 lb. Chrysophenine, 2 lb. phosphate of soda and 10 lb. Glauber's salt. (10) *Lemon Yellow*.—Use 1 oz. Chrysamine G, 2 lb. phosphate of soda and 10 lb. Glauber's salt. (11)

*Yellow*.—Dye with 2 lb. Oxyphenine and 20 lb. salt. (12) *Yellow Olive*.—Use in the dye-bath 2 oz. Cotton brown N, 4½ oz. Diamine bronze G, 4½ oz. Diamine fast yellow B, 3 lb. soda and 20 lb. salt. (13) *Green Yellow*.—Dye with ½ lb.

Diamine fast yellow B, 2 oz. Diamine bronze G, 3 lb. soda and 10 lb. Glauber's salt. (14) *Gold Yellow*.—Use in the dye-bath 3 lb. Columbia yellow, 3 lb. soda and 20 lb. Glauber's salt. (15) *Cream*.—Dye with ½ oz. Toluylene orange G, 24 grains Brilliant orange G, 1 lb. soda and 10 lb. Glauber's salt.

(16) *Primrose*.—Dye with 3 oz. Dianil yellow 3 G, 2 lb. soda and 10 lb. salt. (17) *Gold Yellow*.—Dye with 2½ lb. Dianil yellow G, ½ lb. soda and 15 lb. salt. (18) *Buff Yellow*.—Dye with 3½ oz. Dianil yellow 2 R, ½ lb. soda and 10 lb. salt. (19)

*Orange*.—Prepare the dye-bath with 2 lb. Chlorophenine orange R, 20 lb. common salt. Work at the boil for one hour; lift, rinse and dry. (20) *Red Orange*.—Make the dye-bath with 3 lb. Mikado orange 4 R and 25 lb. salt. Work at the boil for one hour. (21) *Orange*.—Make the dye-bath with 3 lb. Mikado orange G and 25 lb. salt. Work at the boil for one hour. (22) *Pale Orange*.—The dye-bath contains 6 oz. Diamine Orange G, 1½ oz. Diamine fast yellow B, ¼ oz. Diamine scarlet B, 3 lb. soda and 15 lb. Glauber's salt. (23)

*Olive Yellow*.—Dye with ¾ lb. Diamine fast yellow B, 1 oz. Oxydiamine black N, 1½ oz. Diamine bronze G, 3 lb. soda

and 20 lb. Glauber's salt. (24) *Dark Orange*.—Dye with 3 lb. Columbia orange R, 3 lb. soda and 20 lb. Glauber's salt at the boil for one hour. (25) *Bright Orange*.—Use 3 lb. Congo orange R, 3 lb. soda and 20 lb. Glauber's salt at the boil for one hour. (26) *Pale Orange*.—Dye with 3 lb. Dianil orange 2 R, 2 lb. soda and 10 lb. salt at the boil for one hour. (27) *Brilliant Orange*.—Dye with 4 lb. Dianil orange G and 20 lb. salt for one hour. (28) *Deep Orange*.—Dye with 2 lb. Oxydiamine orange R,  $\frac{3}{4}$  lb. soda and 20 lb. salt for an hour. (29) *Pale Orange*.—Dye with  $\frac{3}{4}$  lb. Diamine fast yellow B, 1 lb. Diamine orange B, 3 lb. soda and 15 lb. Glauber's salt. (30) *Bright Orange*.—Dye with  $1\frac{1}{2}$  lb. Benzo orange R,  $1\frac{1}{2}$  lb. Chrysamine R, 10 lb. phosphate of soda and 2 lb. soap.

#### *Direct Dyeing—Greens, etc.*

(1) *Green*.—Prepare the dye-bath with 2 lb. Benzo green G, 10 lb. Glauber's salt. Enter lukewarm, bring slowly to the boil, dye for one hour at the boil. (2) *Russian Green*.—Make the dye-bath with 16 oz. Diamine black HW, 4 oz. Diamine fast yellow A, 3 lb. soda, 15 lb. Glauber's salt, working at the boil for one hour, then lift, wash and dry. (3) *Dark Olive*.—Prepare a dye-bath with  $3\frac{1}{2}$  lb. Benzo olive, 2 lb. Diamine black BO, 2 lb. Diamine yellow, 20 lb. common salt, 2 lb. soap. The goods are entered into the bath at  $160^{\circ}$  F., then heat is raised to the boil, and the dyeing continued for one hour, then lift, wash and dry. (4) *Dark Olive*.—Dye in a bath of 2 lb. Titan yellow Y, 1 lb. Diamine brown Y,  $1\frac{1}{2}$  lb. Diamine blue 3 B, 2 lb. soda. Work for one hour, then lift, wash and dry. (5) *Olive*.—Prepare a dye-bath with 15 lb. phosphate of soda, 3 lb. soap,  $1\frac{1}{2}$  lb. Diamine yellow N, 4 oz. Diamine blue 3 B,  $1\frac{1}{2}$  oz. Diamine brown V. Dye at the boil to shade; lift, wash and dry. (6) *Green Olive*.—Prepare the dye-bath with 1 lb. Diamine black RO, 1 lb. Chrysamine,

$\frac{1}{2}$  lb. Benzo brown, 5 lb. soda, 5 lb. salt, 2 lb. soap. The goods are entered at about 180° F. and worked for a short time, then the temperature is raised to the boil, and the goods are worked for one hour, lifted, washed and dried. (7)

*Reseda*.—Prepare a bath with 10 lb. Glauber's salt, ~~2~~ lb. soap,  $\frac{1}{2}$  lb. Diamine black RO, 2 lb. Diamine yellow N. Enter at 120° F., heat to boil and dye for one hour at that temperature; lift, wash and dry. (8) *Sage Green*.—Prepare a dye-bath with 10 lb. Glauber's salt,  $\frac{1}{2}$  lb. Diamine black RO, 2 lb. Diamine yellow N. Enter at about 150° F., and then raise to boil and dye boiling for one hour, wash and dry.

(9) *Drab*.—Prepare the dye-bath with 10 lb. Cross dye drab, 5 lb. soda crystals. Enter at the boil and work at this temperature for half an hour. Whilst dyeing add gradually 7½ lb. salt. Rinse well and dry. (10) *Olive*.—Prepare the dye-bath with 2 lb. Dianil olive, 5 lb. phosphate of soda, 5 lb. common salt. Dye at the boil for one hour. (11) *Olive*.—

The dyeing is done in a bath containing 4 oz. Diamine black HW,  $1\frac{3}{4}$  lb. Diamine bronze G, 5 lb. soda, 15 lb. Glauber's salt. Work at the boil for one hour. (12) *Grass Green*.—Make the dye-bath with 2 lb. Chrysamine G,  $1\frac{1}{2}$  oz. Benzo azurine G, 3 lb. soap and 10 lb. borax, working at the boil for one hour. (13) *Green*.—Make the dye-bath with 2 lb. Titan yellow Y, 1 lb. Titan blue 3 B and 20 lb. ~~soda~~.

(14) *Bright Grass Green*.—Dye for an hour at the boil with 1 lb. Sulphon azurine D, 2 lb. Thiazole yellow and 20 lb. Glauber's salt. (15) *Green*.—Use in the dye-bath 3 lb. Diamine green B, 3 lb. soda and 20 lb. Glauber's salt, working at the boil to shade. (16) *Dark Green*.—Dye with 3 lb. Diamine dark green N, 3 lb. soda and 20 lb. Glauber's salt. (17) *Green*.—

Use in the bath 3 lb. Benzo green BB, 3 lb. soda and 20 lb. Glauber's salt at the boil for one hour. (18) *Dark Sea Green*.—Dye with 5 oz. Diamine black HW, 3 oz. Diamine catechine G, 3 oz. Diamine fast yellow B, 3 lb. soda and 10 lb.

Glauber's salt. (19) *Pale Green*.—Use in the dye-bath 3 lb. Diamine fast yellow B, 2 oz. Diamine black HW, 3 lb. soda and 10 lb. Glauber's salt. (20) *Bright Pea Green*.—Use in the dye-bath 1 oz. Thioflavine S,  $\frac{1}{2}$  oz. Diamine sky blue FF and 20 lb. Glauber's salt. (21) *Dark Green*.—Use 1 $\frac{1}{2}$  lb. Diamine green G,  $\frac{3}{4}$  lb. Oxydiamine yellow GG, 3 lb. soda and 20 lb. Glauber's salt, working at the boil for one hour. (22) *Deep Green*.—Use 1 $\frac{1}{2}$  lb. Diamine green G,  $\frac{3}{4}$  lb. Diamine black BH,  $\frac{1}{2}$  lb. Oxydiamine yellow GG, 3 lb. soda and 20 lb. Glauber's salt. (23) *Sea Green*.—Use 2 oz. Dianil yellow R, 2 $\frac{1}{2}$  oz. Dianil blue B, 1 $\frac{1}{2}$  oz. Dianil dark blue R, 1 lb. soda and 20 lb. salt, working at the boil. (24) *Leaf Green*.—Dye with 1 $\frac{1}{2}$  lb. Dianil yellow 3 G, 1 lb. Dianil blue B, 11 oz. Dianil blue 2 R, 3 lb. soda, and 20 lb. salt at the boil for one hour. (25) *Deep Green*.—Dye with 2 $\frac{1}{2}$  lb. Dianil yellow 3 G, 2 $\frac{1}{2}$  lb. Dianil blue 2 R, 6 oz. Dianil dark blue R, 3 lb. soda and 20 lb. salt at the boil for one hour. Greens are largely produced by mixing yellows and blues together, as will be seen from the recipes given above ; the particular shade of green which is got from a combination of blue and green depends upon the quality of the dye-stuffs used : thus, to produce bright greens of a pure tone, it is essential that the yellow used shall have a greenish tone like Thioflavine S, Thiazole yellow, or Dianil yellow 3 G, while the blue must also have a greenish tone like Diamine sky blue, Benzo blue 3 B, etc. By using yellows like Diamine fast yellow R, and dark blues like Benzo azurine 3 R, Diamine blue RW, Dianil dark blue R, the green which is got is darker and duller in tone. The addition of such a dye as Diamine black BH throws the shade more to an olive, while a brown dye-stuff, like Diamine brown M, or an orange dye, like Titan orange N, throws the green to a sage tone. Examples of these effects will be found among the recipes given above. It may be added here that by using smaller quantities, but

in the same proportions as given in the above recipes, a great range of tints and shades of green can be dyed from very pale to very deep.

*Direct Dyeing—Blues, etc.*

- (1) *Bright Blue*.—Prepare a dye-bath with  $\frac{1}{2}$  lb. Congo blue 2 B, 5 lb. salt, 5 lb. phosphate of soda, 2 lb. soap. Work at the boil for one hour, then rinse and dry.
- (2) *Dark Navy*.—Prepare a dye-bath with 1 lb. Diamine black RO, 2 lb. Diamine blue 3 R, 8 lb. Glauber's salt, 2 lb. soap. Enter the cotton at  $180^{\circ}$  F., and boil for one hour.
- (3) *Pale Blue*.—Prepare a dye-bath with 10 lb. salt, 3 lb. soda, 3 oz. diamine blue 3 R. Work for one hour at the boil, then lift, wash and dry.
- (4) *Sky Blue*.—Prepare a dye-bath with 2 lb. Titan como G, 20 lb. common salt, 2 oz. acetic acid. Work at the boil for half an hour, then lift, wash and dry.
- (5) *Bright Blue*.—Prepare the dye-bath with  $1\frac{1}{2}$  lb. Chicago blue 6 B, 20 lb. Glauber's salt, 3 lb. soap. Work at the boil for one hour, then lift, wash and dry.
- (6) *Pale Sky Blue*.—Make the dye-bath with 1 oz. Chicago blue 6 B, 10 lb. Glauber's salt, 2 lb. soap. Work at the boil for one hour, then lift, wash and dry.
- (7) *Sky Blue*.—Prepare the dye-bath with 1 lb. Diamine sky blue FF, 1 lb. Turkey-red oil, 20 lb. Glauber's salt. Dye at the boil for one hour.
- (8) *Dark Blue*.—Prepare the dye-bath with  $2\frac{1}{2}$  lb. Diamine blue R,  $2\frac{1}{2}$  lb. Diamine deep black Cr, 1 lb. Turkey-red oil, 40 lb. Glauber's salt. Dye at the boil for one hour.
- (9) *Dark Blue*.—Prepare the dye-bath with 3 lb. Triamine black B, 15 lb. Glauber's salt, in 50 gallons of water. Enter at  $150^{\circ}$  F., and boil for one hour. Allow the goods to remain until the water is cold, when the dye-bath will be completely exhausted.
- (10) *Blue*.—Prepare the dye-bath with 2 lb. Diamine steel blue L, 2 lb. soda, 15 lb. Glauber's salt. Dye at the boil for one hour.
- (11) *Blue*.—Prepare the dye-bath with 4 lb. Diamine blue BG,

2 lb. soda, 20 lb. Glauber's salt. Dye at the boil for one hour. In shade this is very similar to that got with Diamine brilliant blue G, which, however, should be used for light shades on account of its brightness. For deep shades Diamine blue BG is preferable, because of its greater tinctorial power. (12) *Light Indigo Blue*.—Prepare the dye-bath with 1 lb. Paramine indigo blue, 2 lb. soda, 20 lb. Glauber's salt. Enter at about 150° F., and dye at the boil for one hour. (13) *Navy Blue*.—Prepare the dye-bath with 4 lb. Paramine navy blue R, 2 lb. soda, 20 lb. Glauber's salt. Enter at about 150° F., and dye at the boil for one hour. (14) *Blue*.—Prepare the dye-bath with 1 lb. Paramine navy blue R, 2 lb. soda, 20 lb. Glauber's salt. Enter at about 150° F., and dye at the boil for one hour. (15) *Navy Blue*.—Prepare the dye-bath with 4 lb. Benzo chrome black blue B, 15 lb. Glauber's salt, 3 lb. soda. Work at the boil for one hour; lift, rinse and dry. (16) *Grey Blue*.—Prepare the dye-bath with 2 lb. Paramine blue black S, 2 lb. soda, 20 lb. Glauber's salt. Enter at 150° F., and dye for one hour at boil. (17) *Blue*.—Prepare the dye-bath with 1 lb. Paramine blue B, 2 lb. soda, 20 lb. Glauber's salt. Enter at about 150° F., and dye at the boil for one hour. (18) *Slate Blue*.—Prepare the dye-bath with  $\frac{1}{4}$  lb. Diamine black BH,  $\frac{3}{4}$  oz. Diamine fast yellow B, 2 lb. soda and 10 lb. Glauber's salt. Dye at the boil to shade. (19) *Deep Blue*.—Use  $3\frac{1}{4}$  lb. Diamine blue BX,  $\frac{1}{2}$  lb. Oxydiamine black N, 3 lb. soda and 20 lb. Glauber's salt at the boil for one hour. (20) *Blue*.—Dye at the boil for one hour with  $1\frac{1}{2}$  lb. Diamine sky blue, 2 oz. Diamine green B, 2 lb. soda and 10 lb. Glauber's salt. (21) *Navy*.—Dye with 1 lb. Dianil dark blue R, 8 oz. Dianil black CR, 5 lb. soda and 20 lb. Salt at the boil for one hour. (22) *Dark Navy*.—Use 2 lb. Dianil blue R, 2 lb. Dianil dark blue R,  $\frac{3}{4}$  lb. Dianil black CR, 2 lb. soda and 25 lb. salt, working at the boil for one hour. (23) *Deep Blue*.—Dye with  $3\frac{1}{2}$  lb. Diamine blue

black E, 5 lb. soda and 20 lb. Glauber's salt at the boil for one hour. (24) *Deep Blue*.—Dye with 3 lb. Zambesi black BR, 3 lb. soda and 20 lb. Glauber's salt at the boil for one hour. (25) *Dark Navy*.—Use 3 lb. Dianil dark blue R, 3 lb. caustic soda 70° Tw. and 25 lb. salt, working at the boil for one hour. (26) *Violet Blue*.—Dye with 3 lb. Dianil dark blue 3 R and 25 lb. salt at the boil for one hour. (27) *Bright Blue*.—Use 1 lb. Dianil blue B and 20 lb. salt, working at the boil for one hour. (28) *Full Blue*.—Dye with 3 lb. Brilliant azurine 5 G, 5 lb. common salt, 5 lb. phosphate of soda and 2 lb. soap at the boil for one hour. (29) *Dark Blue*.—Dye with 3 lb. Erie blue BX, 3 lb. soda and 20 lb. Glauber's salt at the boil for one hour. (30) *Pale Blue*.—Dye with 1 lb. Chicago blue 6 B, 3 lb. soda and 20 lb. salt at the boil for one hour. (31) *Deep Blue*.—Dye with 1½ lb. Oxydiamine black A, 2 lb. Diamine deep blue R, 3 lb. soda and 20 lb. Glauber's salt at the boil for one hour. (32) *Blue*.—Dye with 6 oz. Diamine blue 3 B, 1½ oz. Diamine sky blue FF, 3 lb. soda and 10 lb. Glauber's salt. (33) *Navy*.—Dye with 4 lb. Diamine new blue R, 3 lb. soda and 20 lb. Glauber's salt at the boil for one hour. (34) *Dark Navy*.—Dye with 1¾ lb. Diamine blue R, 3 lb. soda and 20 lb. Glauber's salt at the boil for one hour. (35) *Sky Blue*.—Prepare the dye-bath with 6 oz. Diamine sky blue FF, 3 lb. soda and 10 lb. Glauber's salt, working at the boil for one hour. (36) *Dark Blue*.—Use in the dye-bath 3 lb. Diamine blue RW, 2 lb. soda and 20 lb. Glauber's salt, working at the boil for one hour. (37) *Dark Blue*.—Prepare the dye-bath with 2 lb. Triamine black BT, and 15 lb. Glauber's salt; work at the boil to shade. (38) *Blue*.—Use 2 lb. Direct indigo blue and 15 lb. Glauber's salt; work at the boil. (39) *Bright Blue*.—Use in the dye-bath 3 lb. Titan comp SN, 2 lb. acetic acid and 20 lb. salt, working at the boil for one hour. (40) *Turquoise Blue*.—Dye with 1 lb. Diamine sky blue, 1 oz. Diamine

fast yellow B, 2 lb. soda and 10 lb. Glauber's salt, working at the boil to shade. (41) *Dark Navy*.—Use 4 lb. Titan Navy R and 20 lb. salt at the boil for one hour. (42) *Green Blue*.—Dye with 1 lb. Dianil blue G, 2½ oz. Dianil yellow G, 1 lb. soda and 20 lb. salt at the boil for one hour. (43) Many more formulæ could have been given, but the above will perhaps suffice; they include all the best of the direct blues. Paler tints of blue may be got by using from 1 to 2 per cent. of any of these blues and also of the many direct blacks now on the market. The direct blues as a rule have a good degree of fastness to light.

#### *Direct Dyeing—Lilacs, Violets, etc.*

- (1) *Lilac*.—Prepare a dye-bath with  $\frac{1}{4}$  lb. Hessian brown 2 M, 1 oz. Azo mauve AM, 1 lb. soap, 2 lb. soda, 10 lb. salt. Work at the boil for one hour, then lift, wash and dry.
- (2) *Plum*.—Dye with 3 lb. Oxydiamine violet G, 3 lb. soda and 20 lb. salt. (3) *Dark Plum*.—Use in the dye-bath 3 lb. Oxydiamine violet B, 3 lb. soda and 20 lb. Glauber's salt, working at the boil. (4) *Violet*.—Make the dye-bath with  $\frac{3}{4}$  lb. Oxydiamine violet B, 1 lb. soda and 10 lb. Glauber's salt, and dye at the boil to shade. (5) *Violet*.—Dye with 12 oz. Dianil blue 4 R, 2 oz. Dianil blue B and 10 lb. salt at the boil. (6) *Lilac*.—Dye with 1½ oz. Diamine rose GD,  $\frac{3}{4}$  oz. Diamine sky blue FF, 1 lb. soda and 10 lb. Glauber's salt at the boil to shade. (7) *Red Violet*.—Make the dye-bath with  $\frac{1}{2}$  lb. Diamine violet N,  $\frac{1}{2}$  oz. Diamine brilliant blue G, 1 lb. soda and 10 lb. Glauber's salt, working at the boil. (8) *Red Violet*.—Dye with 1 lb. Diamine violet N, 1 lb. soda and 10 lb. Glauber's salt. (9) *Bright Red Lilac*.—Dye with 1¾ lb. Erika BN, 4 oz. Chicago blue 4 R, 3 lb. soda and 20 lb. Glauber's salt at the boil. (10) *Grey Lilac*.—Dye with 12 oz. Neutral grey G, 3 oz. Erika BN, 1 lb. soda and 10 lb.

Glauber's salt at the boil for one hour. (11) *Pale Lilac.*—Dye with 2½ oz. Dianil claret B, 2½ oz. Dianil blue 4 R and 10 lb. salt. (12) *Light Plum.*—Dye with 10 oz. Dianil claret B, 10 oz. Dianil blue and 20 lb. salt. (13) *Dull Lilac.*—Dye with ½ lb. Diamine brown V, 1 lb. soda and 10 lb. Glauber's salt. (14) *Heliotrope.*—Dye with 4 oz. Heliotrope 2 B, 1 lb. soda and 10 lb. Glauber's salt. (15) *Plum.*—Dye with 3 lb. Congo Corinth B, 3 lb. soda and 10 lb. Glauber's salt. (16) *Dull Violet.*—Use in the dye-bath 1½ lb. Chicago blue 4 R, 14 oz. Erika BN, 3 lb. soda and 20 lb. Glauber's salt, working at the boil for one hour. (17) *Red Lilac.*—Dye with 6 oz. Oxydiamine violet G, 2 oz. Oxydiamine violet B, 1 lb. soda and 10 lb. Glauber's salt at the boil for one hour. (18) *Violet.*—Dye with 3 oz. Diamine violet N, 2 oz. Diamine blue 3 R, 1 lb. soda and 10 lb. Glauber's salt. (19) *Fawn Drab.*—Prepare a dye-bath with 1 lb. Cachou de laval, ¼ oz. Benzo purpurine B. Enter the cotton into this bath in the cold and heat to the boil, taking about one hour for the operation, then add 4 lb. common salt and boil for three-quarters of an hour longer; lift, wash and dry.

#### *Direct Dyeing—Browns.*

(1) *Pale Olive Brown.*—The dye-bath is made with 1 lb. Diamine bronze G, 1 oz. Cotton brown N, 3 oz. Diamine gold, 5 lb. soda, 15 lb. Glauber's salt. Work at the boil for one hour, then lift, wash and dry. (2) *Red Brown.*—Prepare a dye-bath with 1½ lb. Cotton yellow, 4 lb. Hessian brown 2 BN, 2 lb. Diamine black RO, 1 lb. soda, 2 lb. salt. Enter the goods at 180° F., then raise to the boil and work to the shade; lift, wash and dry. (3) *Brown Drab.*—Prepare a dye-bath with ½ lb. Cotton brown N, ¾ oz. Diamine yellow N, ¾ oz. Diamine black BO, 15 lb. phosphate of soda, 3 lb. soap. Work at the boil for one hour. (4) *Gold Brown.*—

Prepare the dye-bath with 16½ oz. Toluylene orange G, 9½ oz. Toluylene orange R, 4½ oz. Azo mauve, 2½ lb. soap, 5 lb. soda. Dye at the boil for one hour. (5) *Chestnut Brown*.—Prepare a dye-bath with 10 lb. common salt, 2 lb. Benzo brown G, 2 lb. Benzo azurine G, ½ lb. Chrysophenine. Enter the goods at 150° F., raise to the boil and dye boiling for one hour. (6) *Purple Brown*.—Prepare a dye-bath with 10 lb. common salt, 2 lb. Benzo brown NB, 1 lb. Azo violet. Enter the cotton at 150° F., raise to the boil and dye boiling for an hour; lift, wash and dry. (7) *Brown*.—Prepare a dye-bath with 5 lb. soda, 10 lb. Glauber's salt, 12 oz. Chrysamine, 1 oz. Benzo purpurine, 6½ oz. Benzo azurine. Dye at the boil for one hour, rinse and dry. The brown thus got is fast to washing. (8) *Dark Chestnut Brown*.—Prepare a dye-bath with 10 lb. salt, 3 lb. Benzo brown NBX, raise to 150° F., enter goods, heat to boil, and work for one hour; lift, rinse and dry. (9) *Dark Brown*.—Prepare a dye-bath with 20 oz. Glauber's salt per gallon of water used, 2½ lb. soap, 1½ lb. Diamine black RO, 2 lb. Cotton brown N. Enter the yarn at 180° F., give three turns, raise temperature to boil, and work to shade; lift, rinse and wash. (10) *Gold Brown*.—Prepare the dye-bath with 4 lb. Titan gold, 50 lb. salt. Work at the boil for thirty minutes, then lift, wash and dry. The dye-bath is not exhausted, only about 3 lb. of the colour being taken up by the cotton. It may, therefore, be kept for further lots, adding 3 lb. more colour and about 20 lb. more salt for each batch of cotton, or if it is not desired to keep the bath, add less colour to start with, and towards the end of the operation add more salt. (11) *Brown*.—Prepare the dye-bath with 4 lb. Paramine brown G, 20 lb. Glauber's salt, 2 lb. soda. Dye at the boil for one hour. (12) *Light Brown*.—Prepare the dye-bath with 3 lb. Diamine catechine G, 3 lb. soda, 15 lb. Glauber's salt. Dye at the boil for one hour. (13) *Dark Brown*.—Prepare the dye-bath with 5 lb. Diamine catechine

B, 3 lb. soda, 1 lb. Glauber's salt. Dye at the boil for one hour. (14) *Dark Drab*.—Prepare the dye-bath with 1 lb. Titan brown Y, 3 oz. Columbia green,  $32\frac{3}{4}$  oz. Diamine bronze, 17 lb. Glauber's salt. Work at the boil for one hour, then lift, wash and dry. (15) *Pale Brown*.—The dye-bath is made with 2 lb. Mikado orange 4 R, 3 oz. Benzo fast grey, 30 lb. Glauber's salt. Work at the boil for one hour, then lift, wash and dry. (16) *Gold Brown*.—Make a dye-bath with 1 lb. Titan gold, 50 lb. common salt. Enter at the boil, work for an hour, then lift, wash and dry. Keep the bath for another lot of goods; it will only require the addition of about 14 oz. of colour and 10 lb. salt. (17) *Buff Brown*.—Make the dye-bath with  $\frac{3}{4}$  lb. Titan gold,  $\frac{1}{4}$  lb. Titan brown R, 5 oz. Titan blue 3 B, 40 lb. common salt. Work at the boil to shade, then lift, wash and dry. (18) *Deep Chestnut Brown*.—Make the dye-bath with 3 lb. Titan brown R,  $1\frac{1}{2}$  lb. Titan blue R, 25 lb. common salt. Work at the boil for an hour, then lift, wash and dry. (19) *Light Seal Brown*.—Make the dye-bath with 10 lb. salt, 2 lb. soda, 14 oz. Oxyphenine,  $\frac{3}{4}$  lb. Atlas red R, 6 oz. Diamine blue BX. Work at the boil to shade, then lift, wash and dry. (20) *Orange Brown*.—Make a dye-bath with 10 lb. salt, 2 lb. soda, 14 oz. Oxyphenine, 1 lb. Atlas red R, 1 oz. Diamine blue BX. Work at the boil to shade, then lift, wash and dry. (21) *Pale Nut Brown*.—Use in the dye-bath  $4\frac{1}{2}$  oz. Diamine catechine G, 1 oz. Diamine brown M, 1 oz. Diamine catechine B, 2 lb. soda and 10 lb. Glauber's salt, working at the boil for one hour. (22) *Walnut Brown*.—Dye with 1 lb. Diamine brown M, 3 oz. Diamine orange G, 2 oz. Diamine black HW, 2 lb. soda and 10 lb. Glauber's salt at the boil for one hour. (23) *Black Brown*.—Use in the dye-bath 3 lb. Diamine brown M,  $\frac{3}{4}$  lb. Diamine blue black R, 3 lb. soda and 20 lb. Glauber's salt, working at the boil. (24) *Reddish Brown*.—Dye with 2 lb. Dianil brown R, 5 lb. salt and 5 lb. phosphate

of soda at the boil for one hour. (25) *Chocolate Brown*.—Dye with 2 lb. Dianil brown T, 5 lb. phosphate of soda and 5 lb. salt at the boil for one hour. (26) *Dark Brown*.—Dye with 2 lb. Dianil dark brown, 5 lb. salt and 5 lb. phosphate of soda at the boil for one hour. (27) *Light Brown*.—Prepare the dye-bath with 5 lb. Diamine catechine G, 3 lb. soda and 15 lb. Glauber's salt. (28) *Brown*.—Dye with  $2\frac{1}{4}$  lb. Cotton brown N, 4 oz. Diamine black HW, 2 lb. soda and 20 lb. Glauber's salt at the boil for one hour. (29) *Dark Walnut Brown*.—Make the dye-bath with  $3\frac{1}{4}$  lb. Diamine brown M, 6 oz. Diamine catechine B, 6 oz. Diamine red 5 B, 2 lb. soda and 20 lb. Glauber's salt; work at the boil. (30) *Dark Chestnut Brown*.—Dye with  $2\frac{1}{2}$  lb. Dianil brown R, 1 lb. soda and 20 lb. salt at the boil. (31) *Dark Brown*.—Dye with 2 lb. Dianil brown 3 GO, 2 lb. Dianil brown BD, 1 lb. Dianil red 4 B, 3 lb. soda and 25 lb. salt at the boil for one hour. (32) *Brown*.—Prepare the dye-bath with 5 lb. Mikado brown M and 25 lb. salt; work the cotton in this at the boil for one hour. (33) *Nut Brown*.—Use in the dye-bath  $2\frac{1}{2}$  lb. Benzo brown G and 15 lb. salt, working at the boil. (34) *Dark Brown*.—Use in the dye-bath 3 lb. Benzo brown NB and 15 lb. Glauber's salt, working at the boil. (35) *Dark Brown*.—Make the dye-bath with 4 lb. Diphenyl brown BN,  $\frac{1}{2}$  lb. Glauber's salt and 4 lb. soap, working at the boil to shade. (36) *Black Brown*.—Use in the dye-bath  $2\frac{1}{2}$  lb. Dianil brown 3 GO,  $1\frac{1}{2}$  lb. Dianil brown G,  $\frac{3}{4}$  lb. Dianil dark blue R, 3 lb. soda and 25 lb. salt. (37) *Dark Brown*.—Dye with  $1\frac{1}{2}$  lb. Zambesi black D,  $1\frac{1}{4}$  lb. Brilliant orange G, 3 lb. soda and 20 lb. Glauber's salt at the boil to shade. (38) *Gold Brown*.—Dye with 2 lb. Curcumine S, 1 lb. Columbia orange R, 5 oz. Columbia black FB, 3 lb. soda and 15 lb. Glauber's salt at the boil. (39) *Dark Chestnut*.—Dye at the boil with 2 lb. Columbia Orange R, 8 oz. Columbia black FB, 2 lb. soda and 10 lb. Glauber's salt. (40) *Sage Brown*.—Dye with 1 lb.

' Zambesi black D, 1 lb. Curcumine S,  $\frac{3}{4}$  lb. Diamine orange GD, 3 lb. soda and 30 lb. Glauber's salt at the boil. (41) *Deep Brown*.—Dye 3½ lb. Diamine brown M,  $\frac{3}{4}$  lb. Oxydiamine orange G,  $\frac{1}{2}$  lb. Diamine black HW, 3 lb. soda and 20 lb. Glauber's salt at the boil. (42) *Chestnut*.—Dye with  $\frac{21}{2}$  lb. Diamine brown G,  $\frac{3}{4}$  lb. Oxydiamine orange R, 3 lb. soda and 20 lb. Glauber's salt. (43) *Pale Walnut Brown*.—Dye with 3½ lb. Diamine brown M,  $\frac{3}{4}$  lb. Oxydiamine orange G,  $1\frac{1}{2}$  oz. Diamine black BH, 3 lb. soda and 20 lb. Glauber's salt. Various other browns may be obtained by combining the various direct browns together or with other direct dyes. The use of a yellow or orange will brighten them; that of a red will redder the shade; the addition of a dark blue or a black will darken the shade considerably. It may be useful to remember that a combination of red, orange and blue or black produces a brown, and by using various proportions a great range of shades can be dyed.

#### *Direct Dyeing—Blacks.*

- (1) *Black*.—Prepare a dye-bath with 6 lb. Diamine black RO, 2 oz. Thioflavine S, 2 lb. soap, 10 lb. salt. Enter the cotton at the boil and dye for one hour; lift, wash and dry. (2) *Black*.—Prepare the dye-bath with 5 lb. Direct deep black E extra, and  $\frac{1}{2}$  to  $1\frac{1}{2}$  oz. common salt per gallon of water. Dye at the boil for one hour. (3) *Deep Black*.—Prepare the dye-bath with 5½ lb. Diamine deep black RB, 2 lb. soda, 20 lb. Glauber's salt. Dye at the boil for one hour; lift, wash and dry. (4) *Black*.—Prepare the dye-bath with 5 lb. Direct triamine black GX, 15 lb. Glauber's salt. Dye for one hour at the boil; lift, rinse and dry. In working for from two to three hours the dye-bath will exhaust completely. (5) *Black*.—Prepare the dye-bath with 5 lb. Oxydiamine black A, 20 lb. Glauber's salt, 2 lb. soda.

Bye at the boil for one hour. (6) *Black*.—Prepare the dye-bath with 6 lb. Pluto black B. Dye at the boil for one hour with the addition of  $\frac{3}{4}$  to  $1\frac{1}{4}$  oz. Glauber's salt,  $\frac{1}{2}$  to  $\frac{3}{4}$  oz. soda ash per gallon of liquor. To develop the shade it is necessary to dye in a boiling liquor. (7) *Black*.—Use  $2\frac{1}{2}$  lb. Diamine jet black Cr,  $2\frac{1}{2}$  lb. Diamine jet black RB, 2 lb. soda and 20 lb. Glauber's salt, working at the boil for one hour. (8) *Black*.—Use 6 lb. Oxydiamine black NR, 2 lb. soda and 20 lb. Glauber's salt, working at the boil for one hour. (9) *Black*.—Use 6 lb. Columbia black FBB, 3 lb. soda and 20 lb. Glauber's salt, working at the boil to shade. (10) Besides the blacks given in the above recipes, there are other brands which are used in the same way, and vary slightly in the shade of black they give.

#### *Direct Dyeing—Greys, etc.*

All the direct blacks require working in strong baths to give anything like black shades; they all have, more or less, a bluish tone, which can be changed to a jetter shade by the addition of a yellow or green dye in small proportions, which has been done in one of the recipes given above. By coupling, chroming or developing, the direct blacks can be made to give full, deep and fast blacks, and examples of their use in this manner will be found in following sections. By using all the direct blacks in proportions varying from  $\frac{1}{2}$  to 1 per cent. of dyestuff to the weight of the cotton they give greys of various tints and depths; a few examples of such greys will now be given.

(1) *Blue Grey*.—Prepare the dye-bath with  $\frac{1}{2}$  lb. Oxydiamine black A, 1 lb. soda, 10 lb. Glauber's salt. Dye at the boil for one hour. (2) *Bright Grey*.—Prepare a dye-bath with  $4\frac{1}{2}$  oz. Azo mauve AM,  $1\frac{1}{2}$  oz. Direct yellow G, 3 lb. soda, 15 lb. common salt. (3) *Silver Grey*.—Prepare the dye-bath with  $\frac{1}{2}$

- oz. Neutral grey G, 10 lb. sulphate of soda. Work at the boil to shade, then lift, wash and dry. (4) *Slate*.—Dye in a bath with  $\frac{1}{2}$  lb. Diamine black BH, 3 oz. Diamine bronze G, 15 lb. Glauber's salt at the boil for three-quarters of an hour.
  - (5) *Bronze Grey*.—Prepare a dye-bath with  $\frac{1}{2}$  lb. Diamine bronze G, 15 lb. Glauber's salt, 3 lb. soap. Enter at about 160° F., raise to boil and work for one hour; lift, wash and dry.
  - (6) • *Dark Slate*.—Prepare a dye-bath with 10 lb. Glauber's salt,  $1\frac{1}{2}$  lb. soap, 1 lb. Diamine black RO, 2 lb. Cotton brown N. Heat to about 150° F. Enter the goods, work for a short time, then raise to the boil and work for one hour; lift, wash and dry.
  - (7) *Green Grey*.—Prepare a dye-bath with 10 lb. Glauber's salt, 1 lb. Diamine black RO,  $\frac{3}{4}$  oz. Thioflavine S. Enter at from 150° F. to 180° F., raise to boil and dye for one hour; wash and dry.
  - (8) *Light Slate*.—Prepare a dye-bath containing  $2\frac{1}{4}$  lb. soap, 15 lb. Glauber's salt, 6 oz. Diamine black RO,  $\frac{1}{2}$  oz. Thioflavine S. Enter cotton at 140° F., work a little, then heat to boil and dye to shade: lift, wash and dry.
  - (9) *Grey*.—Prepare the dye-bath with  $\frac{1}{2}$  lb. Diamine grey G,  $\frac{1}{2}$  oz. Diamine scarlet B, 1 lb. soda, 1 lb. soap, 5 lb. Glauber's salt. Dye for one hour at the boil.
  - (10) *Light Grey*.—Prepare the dye-bath with 1 lb. Diamine grey G, 1 lb. soda, 1 lb. soap, 5 lb. Glauber's salt. Dye for one hour at the boil; lift, rinse and dry.
- It may be convenient here to deal with the question of the fastness of the direct dyes to such influences as light, air, acids, alkalis, washing and soaping, that have a very material influence on the use of these dyes in dyeing various fabrics.

*Direct Dyes, Fastness to Soap and Light*.—This matter can only be dealt with here in very general terms, for space is limited and the dyes are too numerous for detailed mention. They vary very greatly in degrees of fastness, some are absolutely fast to all influences; the blacks are among the fastest, generally these resist washing and soaping, stand

acids well and are fast to alkalis ; light, however, affects them more or less, though they cannot be reckoned fugitive colours. The few direct greens known are good colours ; they stand washing, soaping and light well, but they are affected by acids and alkalis. The blues vary very much, generally they stand soaping and have a fair degree of fastness to light, acids have but little action, alkalis tend to redder the shade, while heat also affects them. The direct browns are very variable ; they are in general not fast to light ; they stand washing and soaping and resist alkalis, but are altered by acids slightly. The yellows rank among the fastest of colours to light and washing and soaping ; acids have but little effect ; they are reddened by alkalis. Among the reds there is great variation in properties, generally they are not fast to light, standing washing and soaping well and resisting weak alkalis ; some of them, such as the Benzo purpurines and Congo reds, are very sensitive to acids, being turned blue with very weak acids, but on washing or soaping the original colour comes back ; others, like the Titan reds, Diamine reds and Delta purpurines, are not so sensitive, but these are affected by moderately strong acids ; there are a few reds, like Benzo fast scarlet 4 BS and Purpuramine DH, which are fast to acids. The depth of shade which is dyed has some considerable influence on the degree of fastness ; the deeper shades of a colour are always faster than the paler shades, particularly as regards light ; a difference of  $\frac{1}{2}$  per cent. of dyestuff has been known to make a very appreciable degree of difference as regards the fastness of a colour to light.

*Direct Dyeing, Amount of Dye Absorbed.*—In dyeing cotton with all the direct dyes, it is found that the whole of the dyestuff is not removed from the dye-bath ; how much is taken up by the cotton and the depth of the shade which is dyed upon the cotton, chiefly depends upon three factors :

(1) Volume of water used ; (2) Quantity of saline salts used ; (3) Degree of affinity of the dyestuff for the fibre. There are also other factors, such as temperature at which the dyeing is carried on, the character and condition of the fabrics being dyed, etc.

*Ratio of Water to Dye and to Cotton in Dye-bath.—*

The volume of water used in making the dye-bath has a very great influence upon the amount of dye taken up by the cotton, the greater the volume of water the less dye is absorbed and the paler the colour which is produced upon the fibre. It is, therefore, important to use as little water as possible in making up the dye-bath ; indeed, for anything like good results to be obtained with some dyes, especially those of the sulphur series, like Immedial blacks, Katigen browns, Cross-dye blacks, etc., it is necessary to employ what is called a short bath, that is making it as strong as possible. The proportion of water with such dyes should not exceed fifteen times the weight of the cotton being dyed, that is, for every pound of cotton,  $1\frac{1}{2}$  gallons of water can be allowed. This will suit the dyeing of yarns and loose fabrics like knitted stockings and hosiery goods very well. In the case of dyeing piece goods on a jigger or continuous dyeing machines even stronger liquors can be used with advantage. With some of the older direct dyes, like Congo red, Benzo azurine, Diamine scarlets, the proportion of water may be increased to twenty times the weight of the cotton. In any case the quantity of water used should not exceed twenty-five times the weight of the cotton. The second factor, the quantity of saline salts, like Glauber's salt, soda, borax, etc., added in the dyeing, is not without influence, generally the more that is added the more dye there is left in the bath, but here again much depends upon the salt and the colouring matters used. Some salts, more particularly Glauber's salt and common salt, tend to throw

some dyestuffs out of the bath, and so the more there is used of them the deeper the shade produced on the fabric. It is quite impossible, having regard to the scope of this book, to deal with this question in detail. The dyer should ascertain for himself the best salts and the best proportions of these to use with the particular dyes he is using. The recipes given above will give him some ideas on this point. The third factor, the degree of affinity of the dye for the cotton fibre, has some influence on the depth of shade which can be dyed from any given strength of the dye-bath. There is a very considerable difference among the direct dyes in this respect. There are some which have a fair degree of affinity, while there are others which have but little affinity, and while in the former case there is little dye left in the bath, in the latter case there is a good deal. When dyeing plain shades with single dyestuffs this is not of much moment, because if the bath be kept for further use, as will be spoken of presently, the bath may be brought up to its original strength by adding a proportionate amount of dyestuff, but when compound shades are being dyed, using two or more dyes, then this feature has some influence, for they will not be absorbed by the fibre in the same proportion as they were put in the bath, and so when making up the dye-bath for the second lot, and adding the same proportion of dyes, the shade which is produced will not be quite the same, for the first lot of cotton in taking up the dyes in varying quantities has altered their relative proportions, and so the bath for the second lot of cotton will actually contain more of one dye than did the first bath, and the influence of this excess of the one constituent will show itself in the shade ultimately dyed. The more lots of cotton there are dyed in the bath the greater will this influence be. The dyer must by practical experience find out for himself in what direction this feature of the direct dyes exerts its in-

fluence on the particular dyes he is working with and make due allowance. It is found in practice that from one-fourth to one-half of the original weight of dyestuff is left in the bath, and in order to be as economical as possible a custom has arisen of keeping the bath and using it again for dyeing further lots of cotton. In thus making a continuous use of dye-baths it is important in preparing the baths for the next lot of cotton to add first the requisite quantities of dyestuffs, how much will depend upon the factors and conditions already detailed, but from one-half to three-fourths of the original quantities are added. Practical experience alone is the guide to be followed. Having added the dyestuff, then sufficient water must be added to bring up the volume of the bath to the proper amount, for it will have lost some. The loss of water arises from two sources: first there is the evaporation, which always occurs when dye-baths are heated up, and, second, there is the mechanical loss due to its absorption by the material which is being dyed. When a piece of cotton or other textile fabric is immersed in a dye-liquor it absorbs mechanically some of it, and this amount may be roughly put down as about its own weight; thus 100 lb. weight of cotton will take up 10 gallons of liquor and carry that quantity out of the bath. To some extent this may be minimised by a previous wetting out of the cotton which will then have in it as much liquor as it will take up, and so practically no more will be taken up from the dye-bath. Any loss of volume which may thus occur can be remedied by the addition of water. The dye-baths containing in solution, in addition to the dyestuff, salt, or Glauber's salt, or any other added substance, the cotton in taking up the dye-liquor will, of course, take up some of these in proportion to the volume of liquor absorbed. The amount may range from 4 oz. to 1 lb. per gallon of liquor, and if 100 lb. cotton is being dyed and takes up from 10 to 15 gallons of liquor, it is

obvious that it must absorb from 3 to 10 lb. of saline matter, and as the salinity of the dye-liquor is of some importance in dyeing direct colours, in making up the bath for the next lot of cotton this must be allowed for and suitable additions made. In order to do this properly it is a good plan to rely upon the Twaddell test. The dyer should take the Twaddell degree of his bath before use and always make up his baths to that strength. This will be found to range from 3° to 12° Tw. Thus, for instance, a dye-bath made from 120 gallons of water with 20 lb. to 25 lb. common salt or Glauber's salt with the dyestuffs will stand at 4° Tw., one made with 50 lb. common salt or Glauber's salt at 8° Tw., while one which is made with 80 lb. to 100 lb. salt will stand at 12° to 13° Tw. If the dyer always maintains his liquors at one uniform degree Twaddell he can invariably depend upon getting uniform shades from his dye-baths. This uniform strength is attained by adding more salt or more water as the case may require. Of course the continuous working of dye-baths cannot go on for ever; sooner or later the baths become thick and dirty, and then they must be thrown away and a new bath started.

## 2. DIRECT DYEING FOLLOWED BY FIXATION WITH METALLIC SALTS.

It is an acknowledged principle in dyeing that to produce colours fast to washing, soaping and rubbing, there must be produced on the fibre an insoluble coloured substance. Now as the direct dyes do not essentially produce such insoluble bodies when dyed on the cotton, the colours they form are not always fast to washing and soaping. It has been ascertained, however, that some of the direct dyes, e.g. Benzo azurine, Chicago blue, Catechu browns, Diamine blues, Diamine browns, etc., are capable of uniting with metallic

bodies to form insoluble colour lakes, and this combination can take place on the fibre. Fast shades may be dyed with the dyestuffs named above, and with others of this group, by first dyeing them in the usual way, then passing through a boiling bath containing bichromate of potash or copper sulphate, either together or separately. The two fixing agents here named have been found to be the best, although others, as, for instance, zinc sulphate, chromium fluoride and iron sulphate have been tried. With some dyes there is little or no alteration in shade, but in others there is some change, thus the blues as a rule tend to become greener in tone, and browns also tend to acquire a greener tone and deeper shade. The treated shades thus obtained are notable for considerable fastness to washing, soaping and light. It is to be noted that bichromate of potash exercises both a fixing and an oxidising action on dyestuffs, hence it is needful to use it with some degree of caution and not in too great an amount, otherwise with some dyes there is a risk of over-oxidation, and in consequence poor shades will be developed. The following recipes will serve to show what dyes may thus be used, and the colours that can be obtained with them.

*Direct Dyeing and Fixing by Metallic Salts—Reds and Yellows.*

(1) *Dark Red*.—Use in the dye-bath 3 lb. Diamine fast red F, 3 lb. soda and 20 lb. Glauber's salt, work at the boil for one hour, then lift, rinse and pass into a boiling bath containing 3 lb. fluoride of chromium for ten to fifteen minutes, then lift, rinse and dry. By using 1 lb. of the dyestuff in the same way a light red shade is got. (2) *Orange*.—Dye at the boil for one hour with 1 lb. Chrysamine G, 3 lb. soap and 10 lb. Glauber's salt, then rinse and fix in a fresh boiling bath with 1 lb. bichromate of potash, 3 lb. sulphate of copper and

2 lb. acetic acid. (3) *Yellow*.—Dye with  $3\frac{1}{2}$  lb. Diamine yellow N, 3 lb. soap and 15 lb. phosphate of soda, then fix with 4 lb. fluoride of chromium. (4) *Gold Yellow*.—Prepare the dye-bath with 3 lb. Benzo chrome brown 5 G, 1 lb. soda ash, 12 lb. Glauber's salt. Dye at the boil for one hour and rinse. This gives an orange brown. To get the yellow shade, afterwards chrome with 3 lb. bichromate of potash, 3 lb. sulphate of copper, 1 lb. acetic acid, in a fresh bath. Enter at about  $130^{\circ}$  F., bring to the boil, and boil for half an hour.

#### *Direct Dyeing and Fixing by Metallic Salts—Greens.*

(1) *Pale Leaf Green*.—Dye with 3 lb. Dianil yellow 3 G, 1 lb. Dianil yellow R, 1 lb. Dianil blue G and 20 lb. salt, then fix with 3 lb. copper sulphate and 2 lb. acetic acid. (2) *Leaf Green*.—Dye with 3 lb. Dianil yellow 3 G, 3 lb. Dianil blue G and 20 lb. salt, fixing with 4 lb. copper sulphate and 2 lb. acetic acid. (3) *Dark Green*.—Dye with 2 lb. Dianil yellow R,  $1\frac{1}{2}$  lb. Dianil dark blue R, 1 lb. soda and 20 lb. salt, fixing with 3 lb. copper sulphate. (4) *Pale Olive Green*.—Dye with  $2\frac{3}{4}$  lb. Diamine fast yellow B,  $1\frac{1}{4}$  lb. Diamine blue RW,  $\frac{3}{4}$  lb. Diamine blue RW,  $\frac{3}{4}$  lb. Diamine catechine G ; fix with 4 lb. sulphate of copper and 2 lb. acetic acid. (5) *Russia Green*.—Dye with  $2\frac{1}{2}$  lb. Diamine blue RW, 10 oz. Diamine dark blue B,  $2\frac{1}{2}$  lb. Diamine fast yellow B, 3 lb. soda and 20 lb. Glauber's salt ; fix with 4 lb. sulphate of copper and 2 lb. acetic acid. (6) *Blue Green*.—Dye with  $1\frac{3}{4}$  lb. Diamine sky blue FF, 6 oz. Diamine fast yellow B, 1 lb. soda and 10 lb. Glauber's salt ; fix with 2 lb. sulphate of copper and 1 lb. acetic acid. (7) *Bronze Green*.—Use in the bath at the boil 4 lb. Diamine bronze G, 2 lb. soda and 10 lb. Glauber's salt, then fix with 4 lb. fluoride of chromium. (8) *Pea Green*.—Dye in a boiling bath with  $\frac{1}{2}$  lb. Diamine sky blue FF,  $2\frac{1}{4}$  lb. Diamine fast yellow A, 1 lb. soda and 10 lb. Glauber's

salt, then fix in a fresh bath with 2 lb. sulphate of copper and 1 lb. acetic acid. (9) *Leaf Green*.—Dye at the boil for one hour in a bath containing  $2\frac{3}{4}$  lb. Diamine fast yellow B,  $1\frac{1}{4}$  lb. Diamine blue RW, 7 oz. Diamine catechine B, 2 lb. soda and 20 lb. Glauber's salt, then fix in a new bath with 4 lb. sulphate of copper and 2 lb. acetic acid. (10) *Light Green*.—Prepare the dye-bath with  $7\frac{1}{4}$  oz. Diamine blue RW,  $5\frac{1}{2}$  oz. Diamine orange B, 2 lb. Diamine fast yellow B, 1 lb. soda and 10 lb. Glauber's salt, work at the boil for one hour, then treat in a fresh bath with 3 lb. sulphate of copper. (11) *Olive Green*.—Dye with  $2\frac{1}{4}$  lb. Chicago blue RW, 15 oz. Chrysamine G, 2 lb. soda and 10 lb. Glauber's salt; fix with 1 lb. bichromate of potash, 3 lb. sulphate of copper and 2 lb. acetic acid. (12) *Pea Green*.—Use in the dye-bath 3 lb. Chryso-phenine G, 1 lb. Chicago blue 6 B, 2 lb. soda and 10 lb. Glauber's salt, working at the boil for one hour, then fix in a fresh boiling bath with 3 lb. sulphate of copper and 2 lb. acetic acid. (13) *Green*.—Dye with  $2\frac{3}{4}$  lb. Chicago blue 6 B, 5 oz. Chrysamine G, 2 lb. soap and 20 lb. Glauber's salt; fix with 1 lb. bichromate of potash, 3 lb. sulphate of copper and 2 lb. acetic acid. (14) *Dark Green*.—Dye with  $1\frac{1}{2}$  lb. Diamine green B,  $1\frac{1}{2}$  oz. Diamine bronze G, 1 lb. Diamine fast yellow A, 3 lb. soda and 20 lb. Glauber's salt, working at the boil for one hour, then lift, rinse and fix in a fresh boiling bath with 3 lb. fluoride of chromium for one to fifteen minutes. (15) *Dark Bronze*.—Use in the dye-bath  $2\frac{1}{2}$  lb. Diamine bronze G, 3 lb. soda and 20 lb. Glauber's salt, working at the boil for one hour, then lift, rinse and fix with 3 lb. fluoride of chromium as above.

#### *Direct Dyeing and Subsequent Fixing.*

(1) *Dark Blue*.—Prepare the dye-bath with 3 lb. Benzo blue RW, 10 lb. Glauber's salt; dye for one hour at the boil,

then treat in fresh bath with 1 lb. sulphate of copper at the boil for half an hour. (2) *Blue*.—Dye with  $1\frac{3}{4}$  lb. Diamine brilliant blue G,  $1\frac{1}{4}$  lb. Diamine sky blue FF, 2 lb. soda and 20 lb. Glauber's salt; fix in a bath with 4 lb. sulphate of copper and 2 lb. acetic acid. (3) *Light Navy*.—Dye with 1 lb. Diamine blue 3 R,  $2\frac{1}{4}$  lb. Diamine blue RW, 2 lb. soda and 20 lb. Glauber's salt; fix with 4 lb. sulphate of copper and 20 lb. acetic acid. (4) *Bright Navy*.—Dye with 4 lb. Diamine brilliant blue G, 2 lb. soda and 20 lb. Glauber's salt; fix with 4 lb. sulphate of copper and 2 lb. acetic acid. (5) *Blue*.—Dye with 3 lb. Chicago blue RW, 3 lb. soda and 20 lb. Glauber's salt; fix with 3 lb. sulphate of copper and 2 lb. acetic acid. (6) *Dark Blue*.—Dye with 3 lb. Chicago blue RW,  $1\frac{1}{2}$  lb. Zambesi black F, 3 lb. soda and 20 lb. Glauber's salt; fix with 3 lb. sulphate of copper and 2 lb. acetic acid. (7) *Deep Slate Blue*.—Dye with  $1\frac{1}{4}$  lb. Zambesi black F,  $1\frac{1}{4}$  lb. Chicago blue B, 6 oz. Columbia yellow, 3 lb. soda and 20 lb. Glauber's salt; fix with 3 lb. sulphate of copper and 2 lb. acetic acid. (8) *Light Blue*.—Prepare the dye-bath with 2 oz. Diamine sky blue FF,  $\frac{3}{4}$  oz. Diamine fast yellow A,  $\frac{1}{2}$  lb. soda, 2 lb. soap and 5 lb. Glauber's salt dye; for one hour at the boil, then treat in a fresh bath with  $1\frac{1}{2}$  lb. sulphate of copper for half an hour. (9) *Dark Blue*.—Prepare the dye-bath with 4 lb. Behzo chrome black blue B, 15 lb. Glauber's salt and 3 lb. soda. Work at the boil for one hour, then chrome in a fresh bath with 1 lb. bichromate of potash, 1 lb. sulphate of copper and  $\frac{1}{2}$  lb. sulphuric acid. (10) *Dark Blue*.—Dye with  $2\frac{1}{2}$  lb. Diamineral blue R, 3 lb. soda and 20 lb. Glauber's salt; fix with 2 lb. sulphate of copper, 2 lb. bichromate of potash and 2 lb. acetic acid. (11) *Turquoise Blue*.—Dye with 1 lb. Chicago blue 6 B, 2 lb. soda and 10 lb. Glauber's salt, and fix with 3 lb. sulphate of copper and 2 lb. acetic acid. (12) *Dark Turquoise Blue*.—Dye with 3 lb. Chicago blue 4 B, 2 lb. soda and 10 lb. Glauber's salt, and fix

with 3 lb. sulphate of copper and 2 lb. acetic acid. (13) *Black Blue*.—Dye with  $4\frac{1}{2}$  lb. Diamine dark blue B, 1 lb. Diamine new blue R, 2 lb. soda and 10 lb. Glauber's salt, fixing with 5 lb. sulphate of copper and 2 lb. acetic acid. (14) By mixing together the various Diamine blues a very great range of shades can be produced, from pale sky-blue tints to the deepest of blues. (15) *Bright Blue*.—Dye with  $2\frac{1}{4}$  lb. Dianil blue B and 20 lb. Glauber's salt; fix with 3 lb. fluoride of chromium. (16) *Dark Blue*.—Dye with 3 lb. Dianil blue B, 1 lb. Dianil dark blue R, 1 lb. soda and 20 lb. salt, fixing with 3 lb. fluoride of chromium.

#### *Direct Dyeing and Subsequent Fixing—Violets, etc.*

(1) *Red Violet*.—Dye with 1 lb. Dianil blue 4 R and 10 lb. salt, fixing with 4 lb. fluoride of chromium. (2) *Dark Plum*.—Dye with 3 lb. Dianil blue 4 R and 15 lb. salt, fixing with 4 lb. fluoride of chromium. (3) *Red Violet*.—Dye with 1 lb. Diamine blue 3 R, 1 lb. soda and 10 lb. Glauber's salt, fixing with  $1\frac{1}{2}$  lb. sulphate of copper and 1 lb. acetic acid. (4) *Red Plum*.—Use  $3\frac{3}{4}$  lb. Diamine blue 3 R, 3 lb. soda and 20 lb. Glauber's salt, fixing with 5 lb. sulphate of copper and 2 lb. acetic acid.

#### *Direct Dyeing and Subsequent Fixing.*

(1) *Dark Brown*.—Prepare the dye-bath with 5 lb. Diamine catechine B, 3 lb. soda and 15 lb. Glauber's salt, and dye at the boil for one hour, then treat with 2 lb. sulphate of copper and 2 lb. bichromate of potash. (2) *Brown*.—Prepare the dye-bath with 4 lb. Paramine brown G, 20 lb. Glauber's salt, 2 lb. soda and dye at the boil for one hour; treat with 3 lb. copper sulphate. (3) *Light Brown*.—Dye at the boil for one hour in a bath containing 5 lb. Diamine catechine G, 3 lb. soda and 15 lb. Glauber's salt, then treat

in a fresh bath with 2 lb. sulphate of copper and 2 lb. bichromate of potash. (4) *Dark Chestnut Brown*.—Dye for an hour in a boiling bath with  $2\frac{1}{4}$  lb. Diamine catechine G,  $1\frac{1}{4}$  lb. Diamine fast yellow B, 3 lb. soda and 20 lb. Glauber's salt; then fix in a fresh boiling bath with 2 lb. sulphate of copper, 2 lb. bichromate of potash and 2 lb. acetic acid, working for fifteen to twenty minutes, then rinsing and drying. (5) *Brown*.—Use 3 lb. Catechu brown GK, 15 lb. Glauber's salt and  $\frac{1}{2}$  lb. soap; after dyeing for one hour at the boil treat in a fresh boiling bath with 3 lb. copper sulphate. (6) *Dark Brown*.—Dye at the boil for one hour with 3 lb. Catechu brown FK, 15 lb. Glauber's salt and 1 lb. soap, then treat in a fresh boiling bath with 3 lb. copper sulphate. (7) *Brown*.—Prepare the dye-bath with 9 oz. Diamine blue RW,  $12\frac{1}{2}$  oz. Diamine orange B,  $1\frac{3}{4}$  lb. Diamine fast yellow B, 2 lb. soda and 20 lb. Glauber's salt; after working for one hour at the boil treat in a fresh boiling bath with 4 lb. sulphate of copper. (8) *Brown*.—Prepare the dye-bath with 4 lb. Benzo chrome brown 2 R, 20 lb. Glauber's salt (crystals) and dye at the boil for one hour; afterwards treat with bichromate of potash and sulphate of copper. (9) *Nut Brown*.—Dye in a bath with 4 lb. Benzo chrome brown G and 20 lb. salt, then treat in a fresh bath with 4 lb. bichromate of potash, 4 lb. copper sulphate and 1 lb. acetic acid. (10) *Chestnut Brown*.—Dye at the boil for one hour in a bath containing 4 lb. Benzo chrome brown R, and boiling bath with 4 lb. bichromate of potash, 4 lb. sulphate of copper and 1 lb. acetic acid. (11) *Dark Olive Brown*.—Dye with 4 lb. Diamine bronze G, 1 lb. Diamine orange B, 2 lb. soda and 20 lb. Glauber's salt; fix with 5 lb. sulphate of copper and 2 lb. acetic acid. (12) *Deep Brown*.—Use in the dye-bath  $1\frac{3}{4}$  lb. Diamine brown B,  $1\frac{3}{4}$  lb. Diamine fast yellow B,  $\frac{1}{2}$  oz. Diamine black BH, 3 lb. soda and 20 lb. Glauber's salt. The fixing bath contains 2 lb. sulphate of copper, 2 lb. bichro-

mate of potash and 2 lb. acetic acid. (13) *Dark Brown*.—Dye with 2 lb. Diamine brown M, 1 lb. Diamine fast red F,  $\frac{1}{2}$  lb. Diamine jet black Cr, 3 lb. soda and 20 lb. Glauber's salt. The fixing bath contains 2 lb. sulphate of copper, 2 lb. bichromate of potash and 2 lb. acetic acid. (14) *Black Brown*.—Dye with  $1\frac{3}{4}$  lb. Diamine dark blue B,  $\frac{3}{4}$  lb. Diamine orange B,  $1\frac{3}{4}$  lb. Diamine fast yellow B, 2 lb. soda and 20 lb. Glauber's salt, fixing with 5 lb. sulphate of copper and 2 lb. acetic acid. (15) *Light Sage Brown*.—Dye with  $\frac{3}{4}$  lb. Diamine brown B,  $1\frac{1}{2}$  lb. Diamine fast yellow B, 3 oz. Diamine dark blue B, 2 lb. soda and 20 lb. Glauber's salt, fixing with 3 lb. sulphate of copper and 1 lb. acetic acid. (16) *Pale Brown*.—Use in the dye-bath 1 lb. Dianil brown 3 GO, 4 oz. Dianil brown R, 4 oz. Dianil black N, 1 lb. soda and 20 lb. salt, fixing with  $1\frac{1}{2}$  lb. sulphate of copper and 1 lb. acetic acid. (17) *Walnut Brown*.—Dye with  $2\frac{1}{2}$  lb. Diamine blue 3 R, 1 lb. Diamine brown M, 2 lb. soda and 20 lb. Glauber's salt, then fix with 5 lb. sulphate of copper and 2 lb. acetic acid. (18) *Pale Fawn Brown*.—Dye with 2 lb. Diamine blue 3 R, 1 lb. Diamine brown M, 2 lb. soda and 20 lb. Glauber's salt, then fix with 5 lb. sulphate of copper and 2 lb. acetic acid. (19) *Pale Fawn Brown*.—Dye with  $\frac{1}{2}$  lb. Diamine orange B,  $\frac{3}{4}$  lb. Diamine fast yellow B, 1 lb. soda and 10 lb. Glauber's salt, fixing with 2 lb. sulphate of copper and 1 lb. acetic acid. (20) *Sage Brown*.—Dye with 9 oz. Diamine blue RW,  $\frac{3}{4}$  lb. Diamine orange B,  $1\frac{3}{4}$  lb. Diamine fast yellow B, 2 lb. soda; and 20 lb. Glauber's salt. The fixing is done with 4 lb. sulphate of copper and 2 lb. acetic acid. (21) *Red Choco late*.—Dye with 3 lb. Diamine orange B, 1 lb. soda and 10 lb. Glauber's salt; fix with 2 lb. sulphate of copper and 1 lb. acetic acid. (22) *Dark Chestnut*.—Dye with  $2\frac{1}{2}$  lb. Dianil brown 3 GO, 13 oz. Dianil brown R, 13 oz. Dianil brown BD, 1 lb. soda and 20 lb. salt, fixing with 3 lb. copper sulphate and 1 lb. acetic acid. (23) *Brown*.—Dye with  $2\frac{1}{2}$  lb.

Chrysophenine G,  $1\frac{1}{4}$  lb. Diamine brown G,  $1\frac{1}{4}$  lb. Chicago blue RW, 3 lb. soda and 20 lb. Glauber's salt; fix with 3 lb. sulphate of copper and 2 lb. acetic acid. (24) *Nut Brown*.—Dye with 3 lb. Chromanil brown 2 G, 3 lb. soda and 20 lb. Glauber's salt; fix with 1 lb. bichromate of potash, 3 lb. sulphate of copper and 2 lb. acetic acid.

*Direct Dyeing and Subsequent Fixing—Greys.*

- (1) *Dark Grey*.—Dye at the boil for one hour with 1 lb. Zambesi black F, 3 lb. soda and 10 lb. Glauber's salt; fix in a fresh boiling bath with 3 lb. sulphate of copper, 1 lb. bichromate of potash and 10 lb. Glauber's salt. (2) *Dark Grey*.—Dye with 3 lb. Chromanil black 4 RF, 3 lb. soda and 10 lb. Glauber's salt; fix with 1 lb. bichromate of potash, 3 lb. sulphate of copper and 2 lb. acetic acid. (3) *Dark Grey*.—Use in the dye-bath 1 lb. Diamine blue RW,  $\frac{1}{2}$  lb. Diamine orange B,  $\frac{1}{4}$  lb. Diamine new blue R, 2 lb. soda and 20 lb. Glauber's salt, fixing with 4 lb. sulphate of copper and 2 lb. acetic acid. (4) *Pale Greenish Grey*.—Dye with  $\frac{1}{4}$  oz. Diamine orange B, 3 oz. Diamine blue RW,  $\frac{1}{2}$  lb. soda, 2 lb. soap and 5 lb. Glauber's salt, fixing with 1 lb. sulphate of copper and  $\frac{1}{2}$  lb. acetic acid. (5) *Slate Blue*.—Dye with  $\frac{1}{4}$  lb. Diamine dark blue B, 2 oz. Diamine new blue R, 1 lb. soda and 10 lb. Glauber's salt; fix with 2 lb. sulphate of copper and 1 lb. acetic acid. (6) *Grey*.—Prepare the dye-bath with 2 lb. Cross-dye black 2 B, 5 lb. soda ash, 15 lb. common salt; after rinsing leave the cotton in the air to age overnight, rinse again and work for half to three-quarters of an hour at from  $150^{\circ}$  to  $160^{\circ}$  F. in a bath containing 5 lb. bichromate of potash and 5 lb. sulphuric acid, then thoroughly rinse and dry. (7) *Dark Grey*.—Dye with 1 lb. Diamine jet black Cr, 1 lb. soda and 10 lb. Glauber's salt, fixing with 1 lb. bichromate of potash and  $\frac{1}{2}$  lb. acetic acid. (8) *Green Grey*.—Dye

with 1 lb. Diamine dark blue B, 2 oz. Diamine orange B, 4 oz. Diamine fast yellow B, 1 lb. soda and 10 lb. Glauber's salt, fixing with 3 lb. sulphate of copper and 1 lb. acetic acid. (9) *Grey*.—Dye with 4 oz. Dianil black N, 1 lb. soda and 10 lb. salt, fixing with 1 lb. copper sulphate and  $\frac{1}{2}$  lb. acetic acid.

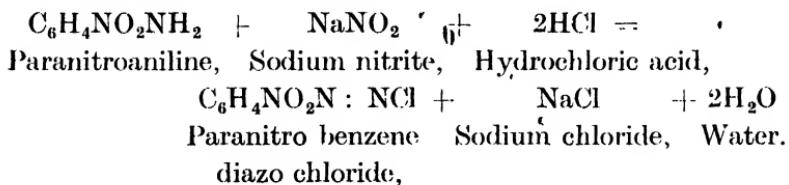
### *Direct Dyeing and Subsequent Fixing—Blacks.*

(1) *Black*.—Prepare the dye-bath with 5½ lb. Diamine jet black RB, 1 lb. Diamine dark blue B, 20 lb. Glauber's salt; dye at the boil for one hour, rinse and then treat the goods simmering for twenty minutes with 4 lb. bichromate of potash. (2) *Black*.—Prepare the dye-bath with 8 lb. Chromanil black RF and 20 lb. Glauber's salt; dye at the boil for one hour, then treat boiling hot for about thirty minutes in a fresh bath with 1 lb. bichromate of potash and 3 lb. sulphate of copper. Add 6 lb. only of the dyestuff to the bath for a second batch. (3) *Black*.—Use 5 lb. Dianil black N, 5 lb. soda and 20 lb. salt; then fix with 3 lb. copper sulphate, 3 lb. bichromate of potash and 2 lb. acetic acid. (4) *Black*.—Use in the dye-bath 5 lb. Dianil black CR, 3 lb. caustic soda, 36° Tw. and 20 lb. salt, fixing with 3 lb. copper sulphate, 3 lb. bichromate of potash and 2 lb. acetic acid. (5) *Jet Black*.—Dye with 5 lb. Diamine jet black Cr, 1 lb. soda and 20 lb. Glauber's salt, fixing with 4 lb. bichromate of potash and 2 lb. acetic acid.

Shades obtained by means of direct dyestuffs may also be made faster to washing (though their fastness to light is sometimes reduced) by after-treating them with formaldehyde. The process is easily carried out since it merely consists of giving the dyed fabric 2-4 ends in a jig containing a 1-2 per cent. solution of formaldehyde at 40°-60° C., subsequently washing and drying the fabric. This treatment is suitable for brown and black colours.

### 3. DIRECT DYEING FOLLOWED BY FIXATION WITH DEVELOPERS.

A large number of the dyes prepared from coal tar are called azo colours, such for instance are the Biebrich and Grecine scarlets and oranges, Naphthol black, Congo red, etc., just to name a few. The preparation of these is about the simplest operation of colour chemistry, and consists in taking as the base an amido compound as the chemist calls such. These amido compounds, of which aniline, toluidine, benzidine, naphthylamine are familiar examples, are characterised by containing the molecular group  $\text{NH}_2$ , which radicle is built up of the two elements nitrogen and hydrogen. All compounds which contain this group are basic in character and combine with acids to form well-defined salts. When these amido bodies are treated with sodium nitrite, and hydrochloric acid they undergo a chemical change, the feature of which is that the nitrogen atoms present in the amido compound and in the nitrite unite and a new compound is produced which is called a diazo compound, and the operation is called "diazotisation." For example, when paranitroaniline is subjected to this reaction it undergoes a change indicated thus:—



The above shows that when paranitroaniline is dissolved with hydrochloric acid and treated with nitrite of soda it forms diazonitro benzene chloride, sodium chloride and water. The diazo compounds are rather unstable bodies, yet they have a great affinity for other compounds, such as naphthol, phenylene diamine, phenol, and combine easily with them.

when brought into contact, the new compounds forming the dyestuffs of commerce. The azo dyes contain the characteristic group of two nitrogen atoms shown in the formula N : N. In dealing with the production of colours direct on the fibre this subject will be elaborated more fully.

Now many of the direct dyes, Diamine blacks, Diamine cutch, Primuline, Diazo brown, Zambesi blues, browns, etc., contain amido groups, by reason of having been made from such bodies as phenylene diamine, amido naphthol, toluidine, etc., and it has been found that when dyed on the fibre they are capable of being diazotised by passing the dyed fibre into a bath of sodium nitrite acidified with hydrochloric acid, and if then they are placed into a bath containing such a body as beta-naphthol, phenylene diamine, etc., new compounds or dyes are produced, which are characterised by being insoluble in water, and, therefore, being formed on the fibre as indicated are very fast to washing, soaping and similar agencies. Often the new or developed dye formed on the fibre differs markedly in colour from the original dye. Perhaps in no case more energetically than with Primuline. The original colour is a greenish yellow, but by using various developers, as they are called, a great variety of shade can be obtained as shown in this table.

<i>Developer.</i>	<i>Colour produced.</i>
Beta-naphthol . . . . .	Bright scarlet.
Alpha-naphthol . . . . .	Crimson.
Phenylene diamine . . . . .	Brown.
Phenol . . . . .	Gold yellow.
Resorcine . . . . .	Orange.
Naphthylamine ether . . . . .	Blue.
Blue developer AN . . . . .	Green.

As regards the dyeing operation, it in no way differs from that described for simple direct colours, yet if good results

are required full shades must be dyed. The cotton must be rinsed in cold water, and be quite cold before being diazotised. *Diazotising* is simple, yet it must be done with care to secure good results. It consists essentially in the use of an acidulated bath of sodium nitrite.

*Preparation of the Acidulated Bath of Sodium Nitrite.*—

To make the bath for diazotising there is taken (for each 100 lb. of goods) sufficient water to handle them in comfortably, 3 lb. of sodium nitrite and 6 lb. hydrochloric acid. This bath must be quite cold otherwise it does not work well. The goods are handled in this for from fifteen to twenty minutes, when they are ready for the next operation. The bath is not exhausted of nitrite, etc., hence it can be kept standing, and for each succeeding lot of cotton it is strengthened up by adding one-third of the quantities of nitrite and acid originally used. Of course the bath cannot be kept for ever, sooner or later it will get dirty, and then it must be thrown away and a new bath be made up.

*Diazo Compounds Formed on Fibre Unstable.*—The diazo compounds formed on the fibre are not very stable bodies. They decompose on being exposed for any great length of time to the air, while light has a strong action on most, if not all of them ; hence it follows that the diazotising process should not be carried out in a room where direct, strong sunlight can enter or fall upon the goods. Then again, after diazotising, the treated goods should not be allowed to lie about exposed to air and light, but the operation of developing should be proceeded with at once, otherwise the diazo body will decompose, and weak and defective colours are liable to be obtained on subsequent development.

*Developers.*—For developing, quite a large number of substances are used. Some of these are regular articles of commerce, others are the special productions of certain firms, who advise their use with the dyes that they also manufac-

ture. These latter are sent out under such designations as *Developer B*, *Developer AN*, or *Fast-blue developer*. Those most in use are (1) beta-naphthol for red from Primuline, and for bluish blacks from Diamine blacks, Diazo blacks, Zambesi blacks, etc.; for dark blues from Diamine blues, Diazo blues, etc.; for greys from Diamine blues, Neutral grey, etc. (2) Alpha-naphthol for dark reds from Primuline, greys from Diamine blues, Neutral grey, etc. (3) Phenylene diamine for blacks from Diamine blacks, Diazo blacks, Zambesi blacks, Triamine blacks, etc.; for dark browns from Diamine browns, Diazo browns, etc.; for light browns from Cotton browns, Diamine cutch, Primuline, etc. (4) Naphthylamine ether for blues from Diamine blacks, etc. (5) Phenol for claret from Diamine cutch, and for gold yellow from Primuline, etc. (6) Resorcine for orange from Primuline, etc. (7) Soda for browns from Diamine cutch, Diazo browns, Zambesi browns, for orange from Diamine orange, and yellow from Primuline.

1. **Beta-naphthol.**—This is by far the most important of the developers. It is a white body, insoluble in water, but readily soluble in soda lye, and a solution is easily made by taking 10 lb. beta-naphthol and heating it with 10 lb. caustic soda lye of 70° Tw. and 60 gallons of water. This bath may be used as the developing bath, or it may be diluted with more water. It is not desirable to use any more caustic soda than is necessary to dissolve the beta-naphthol, so that the bath is not too alkaline. To produce full shades it usually takes 1 per cent. of the weight of the cotton of the beta-naphthol, but it is best to use the bath as a continuous one and for the first lot of cotton use 2 per cent. of naphthol, while for each succeeding lot only 1 per cent. more naphthol need be added to the same bath. This bath is alkaline, while the diazotising bath is acid; unless, therefore, the cotton be well washed when it is taken from the latter bath there is a risk of the alkali of the one being neutralised by the acidity

of the other, and the naphthol being thrown out in an insoluble form. This, of course, is easily remedied should it occur.

**Developer A** (Bayer) is a mixture of beta-naphthol and caustic soda in the powder form, so that a solution is obtained by simply adding water. Rather more (about  $1\frac{1}{2}$  per cent.) of this is required than of beta-naphthol.

2. **Alpha-naphthol Developer** has similar properties to, and is used in the same way as, beta-naphthol ; it develops much darker and rather duller colours, which are less fast to washing.

3. **Resorcine Developer.**—Resorcine, like naphthol, is insoluble in water, but it can be dissolved by using either soda ash or caustic soda. The latter is preferable, as the former is liable to give a developing bath that froths in working, especially if much acid has been left in the cotton from the diazotising bath. The proportions are : 10 lb. resorcine, 25 lb. caustic soda lye of  $70^{\circ}$  Tw., sp. gr. 1.350 and 60 gallons of water ; or 10 lb. resorcine, 20 lb. soda ash and 60 gallons of water, heated until a solution is obtained. In the developing bath 1 per cent. of resorcine is usually sufficient to use. It develops an orange with Primuline.

4. **Developer F** (Bayer) is a mixture of resorcine and soda ash. It requires  $1\frac{1}{2}$  per cent. to make a developing bath.

5. **Phenol Developer**, also known as carbolic acid, finds a use as a developer. It is dissolved in caustic soda, 10 lb. phenol, 15 lb. caustic soda lye of  $70^{\circ}$  Tw., sp. gr. 1.350 and 60 gallons of water. Generally 1 per cent. is sufficient to use as a developer. It is often called yellow developer.

6. **Naphthylamine Ether Developer** is used as a developer for blues in conjunction with the Diamine blacks. It is prepared for use by dissolving in hydrochloric acid, 10 lb. naphthylamine ether powder heated with 5 lb. hydrochloric acid and 50 gallons water. About  $1\frac{1}{4}$  per cent. is required to form a developing bath. Naphthylamine ether is also sent out in

the form of a paste mixed with acid, and containing about 25 per cent. of the actual developer.

7. **Aminodiphenylamine Fast Blue Developer AD** (Cassella) is aminodiphenylamine. It is insoluble in water, but soluble in dilute acid, 10 lb. fast blue developer AD, 5 lb. hydrochloric acid and 35 gallons of water making the bath. To develop full shades 1 to  $1\frac{1}{2}$  per cent. is required.

8. **Blue Developer AN** (Cassella). The base of this is insoluble in water, but dissolves in soda, and is probably a naphthol-sulpho acid. The product, as met with in the market, is soluble in water, and 27 lb. dissolved in 20 gallons of water form the bath. To produce full shades  $1\frac{1}{2}$  per cent. is usually required.

9. **Phenylene Diamine Developer** is most important. It comes into the market in two forms, as a powder, very nearly pure, made into a solution by dissolving 10 lb. with 20 gallons of water and 5 lb. hydrochloric acid, and as a solution prepared ready for use. Developer C (Bayer) and developer E (Bayer) are preparations of diamine, the former in powder, the latter in solution. Phenylene diamine can be used with the addition to the developing bath of acetic acid or soda.

10. **Schaeffer's Acid** is a sulphonic acid of beta-naphthol, and is dissolved by taking 10 lb. of the acid and  $7\frac{1}{2}$  lb. soda, boiling with 50 gallons of water. About  $1\frac{1}{4}$  per cent. is required for developing full shades.

11. **Developer B** (Bayer) is ethyl beta-naphthylamine, in the form of its hydrochloric acid salt. The bath is made from 10 lb. of the developer and 50 gallons of water,  $1\frac{1}{4}$  per cent. being used to obtain full shades.

12. **Developer D** (Bayer) is dioxy-naphthalene-sulphonic acid, and simply requires dissolving in water to make the bath.

13. **Toluylene Diamine** is a homologue of phenylene diamine and is used in precisely the same way. Generally the special developers issued by the various colour firms

simply require dissolving in water to form the developing bath. The cotton, previously being passed through the diazotising bath, is then run into the developing bath, in which it is kept for from twenty to thirty minutes or until the required shade is fully developed, after which it is taken out, rinsed and dried. The method of working is the same for all the developers, and may be carried out in any kind of vessels. As is indicated above, the developing baths may be kept standing and be freshened up as required ; they are used cold. Sometimes two developers are mixed together, in which case care should be taken that an alkaline developer (naphthol or phenol) be not mixed with an acid developer (phenylene diamine, naphthylamine, etc.), unless the acidity of the latter has been neutralised with soda ; otherwise the developer might be thrown out of the bath in an insoluble, and hence useless, form. The advantages of the diazotising and developing process just described may be summed as : easy and quick working, superior fastness to washing, soaping and milling, increased fastness to light and softness of the dyed fibre.

- (1) *Scarlet*.—Dye with 3 lb. Primuline and 20 lb. salt, at the boil for one hour, diazotise and develop with beta-naphthol.
- (2) *Crimson*.—Dye with 3 lb. Primuline and 20 lb. salt, then diazotise and develop with alpha-naphthol.
- (3) *Red Brown*.—Dye with 4 lb. Primuline and 20 lb. salt, then diazotise and develop with phenylene diamine.
- (4) *Deep Orange*.—Dye with 3 lb. Primuline and 20 lb. salt, then diazotise and develop with resorcin.
- (5) *Pale Orange*.—Dye with 3 lb. Primuline and 20 lb. salt, then diazotise and develop with phenol.
- (6) *Sage Brown*.—Dye with 6 lb. Primuline, 3 lb. Titan ingrain blue and 20 lb. salt, then diazotise and develop with resorcin.
- (7) *Dark Maroon*.—Dye with 6 lb. Primuline, 3 lb. Titan ingrain blue and 20 lb. salt, then diazotise and develop with beta-naphthol.
- (8)

*Dark Crimson.*—Dye with  $5\frac{3}{4}$  lb. Primuline,  $\frac{1}{4}$  lb. Titan ingrain blue and 20 lb. salt, then diazotise and develop with beta-naphthol. (9) *Dark Blue.*—Dye with 3 lb. Zambesi blue BX, 2 lb. soda and 20 lb. Glauber's salt, then diazotise and develop with amidonaphthol ether. (10) *Dark Brown.*—Dye with 3 lb. Zambesi brown 2 G, 2 lb. soda and 20 lb. Glauber's salt, then diazotise and develop with toluylene diamine. (11) *Blue Black.*—Dye with 4 lb. Zambesi blue BX, 2 lb. Zambesi black D, 2 lb. soda and 20 lb. salt, then diazotise and develop with  $\frac{3}{4}$  lb. toluylene diamine and  $\frac{1}{2}$  lb. beta-naphthol. (12) *Red.*—Dye with  $4\frac{1}{2}$  lb. Primuline,  $\frac{1}{2}$  lb. Diamine fast yellow A and 20 lb. salt, then diazotise and develop with beta-naphthol. (13) *Dark Brown.*—Dye with 4 lb. Primuline, 1 lb. Diamine azo blue RR and 20 lb. salt, then diazotise and develop with beta-naphthol. (14) *Deep Chestnut Brown.*—Dye with 5 lb. Diamine cutch, 1 lb. soda and 20 lb. Glauber's salt, then diazotise and develop by passing for twenty minutes in a boiling bath of soda. (15) *Dark Brown.*—Dye with 4 lb. Diamine cutch, 1 lb. Diamine black BH, 2 lb. soda and 20 lb. Glauber's salt, then diazotise and develop with phenol. (16) *Black Brown.*—Dye with 1 lb. Diamine brown M,  $1\frac{1}{2}$  lb. Primuline, 1 oz. Diamine black BH, 2 lb. soda and 20 lb. Glauber's salt, then diazotise and develop with Phenylene diamine. (17) *Blue.*—Dye with 2 lb. Diaminogene blue BB,  $\frac{1}{2}$  lb. soda, and 20 lb. Glauber's salt, then diazotise and develop with beta-naphthol. A dark blue is got by using 3 lb. of Diaminogene blue BB in the same way. (18) *Dark Blue.*—Prepare the dye-bath with  $1\frac{1}{2}$  lb. Diaminogene blue BB,  $1\frac{1}{2}$  lb. Diamine azo blue RR, 2 lb. soda, and 20 lb. Glauber's salt. Dye at the boil for one hour, rinse slightly in cold water, then enter into a fresh cold bath prepared with 4 lb. nitrite of soda previously dissolved in water, and  $12\frac{1}{2}$  lb. hydrochloric acid. For subsequent lots in the same bath one-third

of these additions is sufficient. After diazotising rinse the goods in a bath weakly acidulated with hydrochloric or sulphuric acid, and then immediately develop with beta-naphthol. (19) *Black*.—Prepare the dye-bath with 3 lb. Triamine black B, 15 lb. Glauber's salt, in 50 gallons of water. Dye exactly as in the preceding recipe. Wash and rinse very thoroughly after lifting, then diazotise in a bath of about 250 gallons of cold water, to which add separately  $2\frac{1}{2}$  lb. sodium nitrite dissolved in five times its bulk of water and 8 lb. hydrochloric acid diluted. Enter the damp cotton and treat it for about half an hour. Lift, pass through a weak acid bath, rinse, and develop immediately in a bath of about 250 gallons of cold water, containing 1 lb. developer T, 1 lb. soda, previously dissolved together in hot water. Enter the damp goods, work well for half an hour, then lift, wash and dry. (20) *Blue Black*.—Dye with 4 lb. Diamine black BH, 2 lb. soda and 10 Glauber's salt, then diazotise and develop with naphthylamine ether. (21) *Dark Navy*.—Dye with 3 lb. Diamine azo blue RR, 2 lb. soda and 10 lb. Glauber's salt, then diazotise and develop with beta-naphthol. (22) *Light Chestnut Brown*.—Dye with 2 lb. cotton brown N, 1 lb. diamine fast yellow A, 1 lb. soda and 10 lb. salt, then diazotise and develop with phenylene diamine. (23) *Dark Brown*.—Dye with 5 lb. Diamine cutch, 3 lb. soda and 20 lb. Glauber's salt, then diazotise and develop with fast blue developer AD. (24) *Black*.—Dye with 4 lb. Diamine black BH, 3 lb. soda and 20 lb. Glauber's salt, diazotise and develop with 2 lb. resorcine and 1 lb. phenylene diamine. (25) *Blue Black*.—Dye with 4 lb. Diaminogene B, 2 lb. soda and 20 lb. Glauber's salt, then diazotise and develop with beta-naphthol. (26) *Black*.—Dye with  $4\frac{1}{2}$  lb. Diaminogene B,  $\frac{1}{2}$  oz. Diamine fast yellow B, 3 lb. soda and 20 lb. Glauber's salt, then diazotise and develop with 3 lb. resorcine and 1 lb. phenylene diamine.

- (27) *Light Blue*.—Dye with  $1\frac{1}{2}$  lb. Diaminogene blue BB, 1 lb. soda and 10 lb. Glauber's salt, then diazotise and develop with beta-naphthol. (28) *Maroon*.—Dye with 6 lb. Primuline and 20 lb. salt, diazotise and develop with blue developer AN. (29) *Olive Brown*.—Dye with  $5\frac{1}{2}$  lb. Diamine cutch, 3 lb. soda and 10 lb. Glauber's salt, then diazotise and develop with fast blue developer AD. (30) *Gold Brown*.—Dye with 1 lb. Cotton brown N,  $\frac{3}{4}$  lb. Diamine bronze G, 2 lb. soda and 10 lb. Glauber's salt, then diazotise and develop with phenylene diamine. (31) *Walnut Brown*.—Dye with 3 lb. Diamine brown M, 3 lb. soda and 20 lb. Glauber's salt, then diazotise and develop with beta-naphthol. (32) *Brown*.—Dye with  $1\frac{1}{2}$  lb. Diamine brown M, 1 lb. Diamine fast yellow B, 1 lb. Cotton brown N, 1 lb. soda and 10 lb. Glauber's salt, then diazotise and develop with phenylene diamine. (33) *Dark Plum*.—Dye with 3 lb. Diamine brown V, 1 lb. soda and 10 lb. Glauber's salt, then diazotise and develop with beta-naphthol. (34) *Black Brown*.—Dye with 3 lb. Diamine cutch, 3 lb. Diamine black BH, 3 lb. soda and 20 lb. Glauber's salt, then diazotise and develop with phenylene diamine. (35) *Blue Black*.—Dye with  $4\frac{1}{2}$  lb. Diamine black RO, 3 lb. soda and 20 lb. Glauber's salt, then diazotise and develop with beta-naphthol. (36) *Blue Black*.—Dye with  $4\frac{1}{2}$  lb. Diamine black RO, 3 lb. soda and 20 lb. Glauber's salt, then diazotise and develop with naphthylamine ether. (37) *Blue Black*.—Dye with 5 lb. Diamine black BO, 3 lb. soda and 20 lb. Glauber's salt, then diazotise and develop with beta-naphthol. (38) *Dark Blue*.—Dye with 4 lb. Diamine black RO, 3 lb. soda and 20 lb. Glauber's salt, then diazotise and develop with blue developer AN. (39) *Black*.—Dye with 5 lb. Diamine black RO, 1 oz. Diamine bronze G, 3 lb. soda and 20 lb. Glauber's salt, then diazotise and develop with phenylene diamine. The diamine blacks are a range of very useful dyestuffs, and by their means alone

and in conjunction with the various developers, as seen in the examples given above, a range of useful shades of blue, navy-blue, and blacks of every tone can be obtained. It may also be added that many of the direct dyes, although not diazotisable, are not altered by the process and so may be used along with diazotisable dyes for the purpose of shading them, and in that way a great range of shades can be procured, particularly by combining Primuline with other dyes.

#### 4. DIRECT DYEING FOLLOWED BY FIXATION WITH COUPLERS.

A further development in the application of the direct dyes has of late years been made. This is a two-bath method. The cotton is dyed with certain of the direct dyes : Primuline, Diamine jet blacks, Diazo blacks, Toluylene orange and brown, Diazo brown, Diamine nitrazol dyes, Benzo nitrol dyes, etc., in the usual way. Then a bath is prepared by diazotising paranitroaniline, benzidine, metanitroaniline, dianisidine, etc., or by using the ready diazotised preparations which are now on the market, Nitrazol C, Azophor red PN, Azophor blue PN, etc., and immersing the dyed cotton in this bath. Combination takes place between the dye on the fibre and the diazo compound in this bath, and a new product is produced directly on the fibre, which, being insoluble, is very resistant to washing and soaping. These "coupled" shades, as they will probably come to be called, differ from those produced on the fibre by the original dye-stuff, thus the Diamine jet blacks and some of the Diazo blacks give, with paranitroaniline, browns of various shades. In this section also may be considered the method of dyeing cotton by using the direct colours in the ordinary way, and then "topping," as it is called, with a basic dye in a fresh bath.

**Preparation of Diazotised Paranitroaniline.**—Practically

in the "coupling process" of dyeing only diazotised para-nitroaniline is used as the coupler, although other amido bases of a similar nature are available. When paranitro-aniline is used as a source for the coupling bath it is well to prepare a stock bath of diazotised paranitroaniline, which may be done in the following manner :—

*Stock Bath.*—Take 1 lb. paranitroaniline, mix with 1 gallon boiling water and 1 quart hydrochloric acid, stir well, when the paranitroaniline will dissolve; the solution may, if necessary, be assisted by a little heat. Now add  $1\frac{1}{2}$  gallons of cold water, and set aside to cool, when the hydrochloride of paranitroaniline will separate out in the form of fine crystals; when the mixture is quite cold (it cannot be too cold) there is added  $\frac{1}{2}$  lb. sodium nitrite dissolved in  $\frac{1}{2}$  gallon cold water, stir well for fifteen to twenty minutes, by the end of which time the paranitroaniline will have become fully diazotised, cold water is added to bring up the volume of the mixture to 10 gallons. This stock bath, well prepared and kept in a cool, dark place, will keep good for three to four weeks. This bath contains 1 lb. of paranitroaniline in 10 gallons, and it is a good rule to allow  $\frac{1}{2}$  lb. or 5 gallons of this stock bath to each pound of dye-stuff used in dyeing the ground colour to be developed up.

*Coupling Bath.*—To prepare the coupling bath there is taken 5 gallons of the stock bath, 1 lb. sodium acetate with sufficient water for each 1 lb. of dye that has been used. This bath is used cold, and the cotton is worked in it for half an hour, then it is taken out, washed well and dried.

*Use of Nitrazol C.*—Nitrazol C is a ready prepared diazotised paranitroaniline in a powder form which keeps well if stored in a dry place. The method of using is to take 8 lb. Nitrazol C, stir into a paste with water, and then add this paste to the coupling bath, together with 2 lb. soda and  $\frac{3}{4}$  lb. acetate of soda. This bath is used cold and the dyed cotton

- 2 lb. Primuline, 1 lb. Diamine jet black OO and 20 lb. salt. (20) *Chocolate*.—Dye with 1½ lb. Diamine brown V, 2 lb. Diamine nitrazol brown RD, 2 lb. soda and 20 lb. Glauber's salt. (21) *Olive Brown*.—Dye with 2 lb. Diamine nitrazol brown G, 1 lb. Diamine nitrazol black B, 1 lb. soda and 20 lb. Glauber's salt. (22) *Russian Green*.—Dye with 2 lb. Diaminogene extra, 2 lb. soda and 20 lb. Glauber's salt. (23) *Bronze Green*.—Dye with 2 lb. Diamine grey, 2 lb. soda and 20 lb. Glauber's salt. (24) *Terra-cotta Red*.—Dye with 2 lb. Oxydiamine orange R, 1 lb. soda and 20 lb. Glauber's salt. (25) *Terra-cotta Brown*.—Dye with 2 lb. Diamine nitrazol brown RD, 1 lb. soda and 20 lb. Glauber's salt. (26) *Olive Green*.—Dye with 1 lb. Primuline, 2 lb. Diamine bronze G, 1 lb. soda and 20 lb. Glauber's salt. (27) *Dark Green*.—Dye with 1 lb. Primuline, 2 lb. Diamine nitrazol black B, 2 lb. soda and 20 lb. salt. (28) *Sage Brown*.—Dye with 1 lb. Primuline, 2 lb. Diamine jet black OO, 1 lb. soda and 20 lb. salt. (29) *Black Brown*.—Dye with 1 lb. Diamine brown V, 2 lb. Diamine nitrazol black B, 2 lb. soda and 20 lb. Glauber's salt. (30) *Dark Walnut*.—Dye with 1 lb. Diamine brown V, 2 lb. Oxydiamine orange R, 2 lb. soda and 20 lb. Glauber's salt. (31) *Pale Sage*.—Dye with 1 lb. Diamine brown V, 2 lb. Primuline, 1 lb. soda and 20 lb. salt. (32) *Brown*.—Prepare the dye-bath with 3 lb. Diamine jet black OO, 20 lb. Glauber's salt, 2 lb. salt, 2 lb. soda. Dye at the boil for one hour. (33) *Brown*.—Prepare the dye-bath with ¾ lb. Benzo nitrol brown G, 20 lb. Glauber's salt, 2 lb. soda. Dye for one hour at the boil. (34) *Dark Brown*.—Prepare the dye-bath with 2 lb. Benzo nitrol dark brown N, 20 lb. Glauber's salt, 2 lb. soda. Dye for one hour at the boil. (35) *Brown*.—Prepare the dye-bath with 4 lb. Direct fast brown B, 20 lb. Glauber's salt, 2 lb. soda. Dye for one hour at the boil. (36) *Brown*.—Prepare the dye-bath with 1 lb. 11 oz. Diamine jet black OO, 2 lb. Cotton brown N,

- 1 lb. 5 oz. Diamine brown V, 20 lb. Glauber's salt, 2 lb. soda. Dye at the boil for one hour. (37) *Brown*.—Prepare the dye-bath with 2 lb. Diamine bronze G, 6½ oz. Cotton Brown N, 9¾ oz. Diamine fast yellow A, 20 lb. Glauber's salt, 2 lb. soda. (38) *Black*.—Prepare the dye-bath with 5 lb. Pluto black B, 20 lb. Glauber's salt, 2 lb. soda. Dye for one hour at the boil.

*Solidogen A Coupling Bath*.—Solidogen A is a coupler that has latterly been applied. It is a syrupy liquid, and the coupling bath is made by taking from 4 lb. to 6 lb. of the Solidogen A, and 1 lb. to 2 lb. of Hydrochloric acid, in place of which 3 lb. to 5 lb. alum may be used. This bath is used at the boil, the goods being treated for half an hour, then well rinsed and dried. It increases the fastness of the colours to washing and soaping. The following recipes show its application : (1) *Bright Red*.—Dye with 3 lb. Dianil red 4 B, 2 lb. soap, 3 lb. soda and 15 lb. Glauber's salt, then fix with Solidogen A. (2) *Scarlet*.—Dye with 3 lb. Dianil scarlet G, 2 lb. soda and 25 lb. salt ; fix with Solidogen A. (3) *Plum*. Dye with 3 lb. Dianil claret B, 5 lb. soda and 10 lb. Glauber's salt, then fix with Solidogen A.

**Topping with Basic Dyes**.—The shades dyed with the direct dyes may be materially brightened and new shades produced by topping with any of the basic dyes, which are applied in a fresh warm bath. A great variety of effects may be thus obtained, of which the following recipes give a few examples : (4) *Green*.—Dye with 1 lb. Titan yellow G and 20 lb. salt ; top with ½ lb. Brilliant green. (5) *Blue*.—Dye with 1½ lb. Diamine azo blue R, 1 lb. soda and 20 lb. Glauber's salt, then top with 2 oz. New Methylene blue N. (6) *Bright Blue*.—Dye with ¾ lb. Diamine brilliant blue G, 1 lb. soda and 10 lb. Glauber's salt ; top with 2 oz. New Methylene blue 3 R. (7) *Blue*.—Dye with 1 lb. Diamine sky blue, 1 lb. soda and 10 lb. Glauber's salt, and top with 4 oz. Brilliant

green. (8) *Rose Lilac*.—Dye with  $1\frac{1}{2}$  oz. Diamine violet N, 1 lb. soda and 10 lb. Glauber's salt, then top with 2 oz. Tannin heliotrope. (9) *Green*.—Dye at the boil for one hour with 2 lb. Benzo green G and 10 lb. Glauber's salt, then top in a fresh bath with  $\frac{1}{2}$  lb. Turquoise blue BB. (10) *Violet*.—Dye with 5 oz. Diamine violet N, 2 oz. Diamine brilliant blue G, 1 lb. soda and 10 lb. salt, and top with 1 oz. Methyl violet 2 B. (11) *Plum*.—Dye with  $1\frac{1}{2}$  lb. Oxydiamine violet B, 5 oz. Diamine red 10 B, 2 lb. soda and 10 lb. Glauber's salt, then top with  $1\frac{1}{2}$  oz. Methyl violet R. (12) *Bright Green*.—Dye with  $1\frac{1}{4}$  lb. Diamine green G,  $1\frac{1}{4}$  lb. Oxydiamine yellow GG, 2 lb. soda and 10 lb. Glauber's salt, then top with 2 oz. Brilliant green. (13) *Blue*.—Dye with 2 lb. Benzo azurine G, 3 oz. Brilliant azurine B, 1 lb. soda and 20 lb. Glauber's salt, topping with 6 oz. Turquoise blue G and 3 oz. New Victoria blue B. (14) *Dark Lilac*.—Dye with  $3\frac{3}{4}$  lb. Heliotrope BB, 1 lb. soda and 20 lb. Glauber's salt, then top with 1 lb. Methyl violet R, and  $\frac{1}{2}$  lb. Methyl violet 3 R. (15) *Scarlet*.—Dye with 3 lb. Brilliant Congo R, 3 lb. soda and 20 lb. Glauber's salt, then top with 8 oz. Safranine. (16) *Bright Green*.—Dye with 3 lb. Chrysamine G, 2 lb. soap and 10 lb. phosphate of soda, topping with  $\frac{3}{4}$  lb. Malachite green. (17) *Bright Violet*.—Dye with  $1\frac{1}{2}$  lb. Chicago blue 6 B, 1 lb. soda and 20 lb. Glauber's salt, topping with 10 oz. Methyl violet B. (18) *Dark Green*.—Dye with 2 lb. Columbia green, 3 lb. soda and 10 lb. Glauber's salt, topping with 10 oz. Malachite green. (19) *Claret*.—Prepare a dye bath with  $\frac{3}{4}$  oz. Diamine black RO,  $2\frac{1}{2}$  lb. Benzo Purpurine 6 B, 10 lb. Glauber's salt. Dye at the boil for one hour, then enter in a fresh cold bath of  $\frac{1}{2}$  lb. Safranine G. Work for twenty minutes, lift, wash, and dry. (20) *Seal Brown*.—Make up a dye-bath with 2 lb. Benzo azurine G, 20 lb. Glauber's salt. Enter yarn at  $180^{\circ}$  F., dye at the boil for one hour, lift, wring, and enter into a fresh bath of  $1\frac{1}{2}$  lb.

Bismarck brown. Work for one hour at about 180° F., lift, rinse well, and dry.

### 5. DYEING ON TANNIC AND KATANOL MORDANTS.

**Basic Dyes.**—The oldest group of coal-tar dyes are the basic dyes, of which Magenta, Brilliant green, Chrysoidine, Bismarck brown, Auramine are typical representatives. For a long time these dyes were only used for dyeing wool and silk; for cotton, linen, and some other vegetable fibres they have little or no affinity, and hence cannot dye them direct. However, it was found out that if the cotton be prepared or mordanted (as it is called) with tannic acid or with any substance containing that compound, they could be used for dyeing cotton.

The mordant used, tannic acid, has the property of combining with the dyes of this group to form insoluble coloured tannates. Now tannic acid has a certain amount of affinity for cotton: if the latter be immersed in solution of tannic acid, or any material containing it, some of the latter is taken up and more or less fixed by the cotton fibre. Tannic acid is a vegetable product found in a large number of plants and plant products, such as sumac, myrabolans, divi-divi, galls, oak bark, gambier, cutch, etc., which are commonly known as tannins, or tannin matters, on account of their use in the conversion of animal skins or hides into leather, which is done in the tanning industry. By itself the tannin-colour lake, which may be formed on the cotton fibre by immersion first in a bath of tannin and then in a dye-bath, is not fast to washing and soaping, but by taking advantage of the fact with such metals as tin, iron, antimony, etc., it combines to form insoluble tannates; the tannic acid can be fixed on the cotton by immersion in a bath containing such fixing salts as tartar emetic, tin crystals, copperas, antimony

fluoride and antimony oxalate. The dyeing of cotton with the basic colours, therefore, resolves itself into three operations : (1) Tanning with tannic acid or some tanning matters. (2) Fixation with tartar emetic or other fixing agent. (3) Dyeing with the required colour or mixture of colours.

1. **The Tanning Operation.**—The practice of tanning or mordanting cotton with tannin is variously carried out by dyers. Some steep the cotton in the tannin bath over night, others immerse it from two to three hours in a luke-warm bath, while some enter it in a boiling bath, which is then allowed to cool down and the cotton is lifted out. The last is perhaps the quickest method, and experiments have shown that it is as good as any other method, if the quantity of tannic acid taken up be regarded as the criterion of success. In the natural products which have just been enumerated, the tannic acid is accompanied by some colouring matter, which is also absorbed by the cotton ; in some (sumac and galls) this colour is present in but small quantities : in others (divi-divi, myrabolams), there is a large quantity : therefore cotton treated with these comes out more or less coloured. Now it is obvious that such forms of tannin cannot be used when light tints are to be dyed, for such the acid itself must be used, for medium shades sumac or galls may be used ; while when dark shades—browns, maroons, dark greens, navy-blues, etc.—are to be dyed, then such tannin matters as divi-divi or myrabolams may be conveniently and economically adopted. The quantity used varies according to circumstances ; the character of the shades that are to be dyed, the dyestuff used, the quality and character of the tannin matter used. For pale shades about 1 per cent. of tannic acid may be used ; deep shades require from 3 to 4 per cent. Of tannin matters from 5 per cent. may be used for pale shades, from 20 to 25 per cent. for deep shades. The tannin baths are not

exhausted and may be kept standing, adding for each succeeding lot of cotton from  $\frac{1}{2}$  to  $\frac{3}{4}$  of the above quantities of tannin matters. Of course sooner or later the baths become unusable from various causes, and then they may be thrown away; but old tannin baths often work better than the new ones.

**2. The Fixing Bath.**—Following on the tannin bath comes the fixing bath to fix the tannin on the cotton in the form of insoluble metallic tannates. A variety of metallic salts may be used for this purpose, those of antimony, tin, iron, lead, etc., the substances most commonly used being tartar emetic, antimony fluoride, oxalate of antimony, tin crystals and copperas. Beyond forming the insoluble tannate of antimony or tin, as the case may be, the salts of antimony and tin have no further effect on the tanned cotton, and they may be used to fix the tannin for all tints or shades, from very pale to very deep. Of all these salts tartar emetic has been found to be the best, probably because it is the least acid in its reactions, and therefore there is no tendency to remove any tannin from the fibre, as is the case with the other salts. Tin salt is little used for this purpose, because of its acidity, which prevents it from fixing the tannin as completely as is the case with tartar emetic. With copperas or iron liquor the question comes up not only of the mere fixation of the tannin, but also the fact that iron forms with tannin grey to black compounds, hence cotton which has been tanned and then immersed in a bath of copperas becomes coloured grey to black, according to the quantity of the tannin matter used. The property is useful when dark shades of maroons, clarets, greens, browns, blues, etc., are to be dyed, and is frequently employed.

Katanol is the most recent mordant suitable for use in the dyeing of basic colours on cotton. It is a sulphurised

phenol product and therefore has some relationship to a sulphur dyestuff.

Katanol is insoluble in acids but easily soluble in sodium carbonate. Hence, in mordanting, cotton is given several ends in a hot bath prepared by dissolving 3 parts of Katanol with 2 parts of sodium carbonate in hot water, salt being added in the later stages. After washing, the fabric is then ready for dyeing in the usual manner with a basic colour. The amount of Katanol required is usually 3 to 6 per cent., calculated on the weight of the cotton.

On the whole, dyeings obtained by means of Katanol are equally fast to light and washing as those obtained by the aid of tannic acid.

**3. Dyeing.**—After the mordanting operations comes the dyeing. This is not by any means a difficult operation. It is best carried out by preparing a cold bath, entering the prepared or mordanted cotton in this and heating slowly up. It is not necessary to raise to the boil nor to maintain the dye-bath at that heat, a temperature of 180° F. being quite sufficient in dyeing with the basic colours, and the operation should only last until the colouring matter is extracted from the dye-bath. Working in this way, level uniform shades can be obtained. One source of trouble in the dyeing of basic dyes, more especially with magentas, violets and greens, lies in their slight solubility and great strength. In preparing solutions of such dyes it is best to dissolve the dyestuff together with a small amount of acetic acid by pouring boiling water over it, and stirring well until all appears to be dissolved. This solution should be strained through a fine cloth, as any undissolved specks will be sure to fix themselves on the cloth and lead to dark spots and stains, as, owing to the weak solubility of the dye, and this being also fixed as insoluble tannate by the tannic acid on the fibre, there is no tendency for the dye to diffuse itself.

over the cloth, as occasionally happens in other methods of dyeing. No advantage is gained by adding to the dye-bath such substances as common salt or Glauber's salt, but the addition of acetic acid is beneficial since it aids the solubility of the dyestuff. Some few of the dyes, e.g. Soluble blue, Victoria blue, which will dye on a tannic mordant, are sulphonated compounds of the colour base. These can be dyed in medium or light shades on to unmordanted cotton from a bath containing alum, and in the ordinary method of dyeing the addition of alum is beneficial, as tending to result in the production of deep shades. These are somewhat faster to washing and soaping, which is owing to the dyestuff combining with the alumina in the alum to form an insoluble colour lake of the sulphuric acid groups it contains. Many recipes can be given for the dyeing of basic dyes on cotton; for the range of tints and shades of all colours that can be produced by their means is truly great. Typical recipes will be given showing what basic dyes are available and how they can be combined together. The dyer, however, who knows how to produce shades by combining one dyestuff with another is able to get many more shades than space will permit to be given here. (1) *Sky Blue*.—Mordant with 1 lb. tannic acid and  $\frac{1}{2}$  lb. tartar emetic, then dye with  $2\frac{1}{2}$  oz. Victoria blue B and  $\frac{1}{2}$  oz. Turquoise blue G. (2) *Bright Blue*.—Mordant with 2 lb. tannic acid and  $1\frac{1}{2}$  lb. tartar emetic, then dye with  $1\frac{1}{2}$  lb. New Victoria blue B and  $\frac{3}{4}$  lb. Turquoise blue G. (3) *Pale Green*.—Mordant with  $1\frac{1}{2}$  lb. tannic acid and  $\frac{1}{4}$  lb. tartar emetic, then dye with  $\frac{1}{4}$  oz. Brilliant green and  $\frac{1}{2}$  oz. Auramine II. (4) *Bright Green*.—Mordant with 1 lb. tannic acid and 1 lb. tartar emetic, then dye with 6 oz. Brilliant green and 8 oz. Auramine II. (5) *Turquoise Blue*.—Mordant with 2 lb. tannic acid and  $1\frac{1}{2}$  lb. tartar emetic; dye with 1 lb. Turquoise blue G. (6) *Crimson*.—Mordant with 3 lb. tannic

acid and 2 lb. tartar emetic, then dye with  $1\frac{1}{4}$  lb. Brilliant rhoduline red B and 5 oz. Auramine II. (7) *Bright Violet*.—Mordant with 2 lb. tannic acid and 1 lb. tartar emetic; dye with  $1\frac{1}{4}$  lb. Rhoduline violet and 3 oz. Methyl violet B. (8) *Rose Lilac*.—Mordant with 2 lb. tannic acid and 1 lb. tartar emetic; dye with  $\frac{3}{4}$  lb. Rhoduline violet. (9) *Yellow*.—Mordant with 3 lb. tannic acid and  $2\frac{1}{2}$  lb. tartar emetic; dye with 2 lb. Auramine II. (10) *Orange*.—Mordant with 3 lb. tannic acid and  $2\frac{1}{4}$  lb. tartar emetic; dye with 2 lb. Chrysoidine. (11) *Green*.—Mordant with 3 lb. tannic acid and  $2\frac{1}{2}$  lb. tartar emetic, then dye with 2 lb. Brilliant green. (12) *Red Violet*.—Mordant with  $1\frac{1}{2}$  lb. tannic acid and  $1\frac{1}{4}$  lb. tartar emetic, then dye with 8 oz. Methyl violet 4R. The same method may be followed with all the brands of Methyl, Paris and Hoffmann violets, and so a range of shades from a purple to a pure violet can be dyed. The 4R to R brands of these violets dye reddish shades, the redness decreasing according to the mark, the B to 6B brands dye bluish shades, the blueness increasing till the 6B brand dyes a very blue shade of violet. (13) *Bright Sea Green*.—Mordant with 1 lb. tannic acid and  $\frac{1}{2}$  lb. tartar emetic, then dye with 2 oz. Turquoise blue G and  $\frac{1}{4}$  oz. New Victoria blue B. With these two blues a very great variety of tints and shades of blue can be dyed. (14) *Sea Green*.—Mordant with 1 lb. tannic acid and  $\frac{3}{4}$  lb. tartar emetic, and dye with 2 oz. Malachite green. (15) *Dark Green*.—Mordant with 3 lb. tannic acid and 2 lb. tartar emetic, then dye with  $1\frac{1}{4}$  lb. Malachite green and  $\frac{3}{4}$  oz. Auramine II. (16) By combination of Brilliant green or Malachite green (which are the principal basic greens) with Auramine in various proportions a great range of greens of all tints and shades, from pale to deep and from very yellow to very green tints, can be dyed. (17) *Scarlet*.—Mordant with 3 lb. tannic acid and 2 lb. tartar emetic, then dye with  $1\frac{1}{2}$  lb. Rhodamine 6G and  $\frac{1}{4}$  lb. Ara-

mine II. (18) *Pink*.—Mordant with 1 lb. tannic acid and  $\frac{3}{4}$  lb. tartar emetic, and dye with  $\frac{1}{4}$  lb. Rhodamine G. (19) *Pink*.—Mordant with 1 lb. tannic acid and  $\frac{3}{4}$  lb. tartar emetic, and dye with  $\frac{1}{2}$  lb. Irisamine G. (20) *Slate Blue*.—Mordant with  $1\frac{1}{2}$  lb. tannic acid and 1 lb. tartar emetic, then dye with  $\frac{3}{4}$  lb. Victoria blue B and 2 oz. Malachite green. (21) *Indigo Blue*.—Mordant with 3 lb. tannic acid and  $2\frac{1}{2}$  lb. tartar emetic, then dye with 1 lb. Methylene blue 2B and  $\frac{1}{2}$  lb. Malachite green. (22) *Dark Scarlet*.—Mordant with 3 lb. tannic acid and  $2\frac{1}{2}$  lb. tartar emetic, then dye with 1 lb. Safranine prima and  $\frac{1}{2}$  lb. Auramine II. (23) *Grey*.—Mordant with 1 lb. tannic acid and  $\frac{1}{2}$  lb. tartar emetic, then dye with  $\frac{1}{2}$  lb. New Methylene grey B. (24) *Bluish Rose*.—Mordant with 2 lb. tannic acid and 1 lb. tartar emetic, then dye with 1 lb. Rhodamine B. (25) *Maroon*.—Mordant with 4 lb. tannic acid and 2 lb. tartar emetic, and dye with 2 lb. Magenta and  $\frac{1}{2}$  lb. Auramine. (26) *Dark Green*.—Mordant with 5 lb. tannic acid and  $2\frac{1}{2}$  lb. tartar emetic, and dye with  $\frac{1}{2}$  lb. Methylene blue BB,  $\frac{1}{2}$  lb. Methyl violet 2B and  $2\frac{1}{2}$  lb. Auramine II. (27) *Orange*.—Mordant with 3 lb. tannic acid and  $2\frac{1}{2}$  lb. tartar emetic, and dye with 1 lb. New Phosphine G. (28) *Lilac Grey*.—Mordant with 1 lb. tannic acid and  $1\frac{1}{2}$  lb. tartar emetic, and dye with  $\frac{1}{4}$  lb. Methylene grey BF. (29) *Gold Brown*.—Mordant with 3 lb. tannic acid and  $1\frac{1}{2}$  lb. tartar emetic, and dye with  $\frac{3}{4}$  lb. Thioflavine T and  $\frac{3}{4}$  lb. Bismarck brown. (30) *Orange*.—Mordant with 2 lb. tannic acid and 1 lb. tartar emetic, and dye with 1 lb. Auramine and  $\frac{1}{4}$  lb. Safranine. (31) *Dark Blue*.—Mordant with 3 lb. tannic acid and 2 lb. tartar emetic, and dye with  $2\frac{1}{2}$  lb. New Methylene blue R and  $\frac{3}{4}$  lb. Naphtindone BB. (32) *Olive Green*.—Mordant with 5 lb. sumac extract and 2 lb. copperas, and dye with 1 lb. Ajramine. (33) *Russian Green*.—Mordant with 5 lb. sumac extract and 2 lb. copperas, and dye with 2 lb. Malachite green. (34) *Scarlet*.—Mordant with 3 lb. tannic

acid and 2 lb. tartar emetic, and dye with  $1\frac{1}{2}$  lb. Thioflavine T and  $\frac{1}{2}$  lb. Irisamine G. With these two dyestuffs it is possible to produce a variety of useful shades from a pure greenish yellow, with Thioflavine T alone, to a bright bluish pink, with the Irisamine alone, through orange, scarlet, etc., with combinations of the two dyestuffs. (35) *Dark Grey*.—Mordant with 5 lb. sumac extract and 3 lb. copperas, then dye with 1 lb. New Methylene grey G. (36) *Blue Black*.—Mordant with 8 lb. sumac extract and 4 lb. copperas, or better with iron liquor, then dye with 2 lb. Indamine blue N. (37) *Olive Brown*.—Mordant with 5 lb. sumac extract and 3 lb. copperas, and dye with  $1\frac{1}{2}$  lb. New Phosphine G. (38) *Indigo Blue*.—Mordant with  $1\frac{1}{2}$  lb. tannic acid and 1 lb. tartar emetic; dye with  $\frac{1}{2}$  lb. New Methylene blue N. (39) *Sky Blue*.—Mordant with  $\frac{1}{2}$  lb. tannic acid and  $\frac{3}{4}$  lb. tartar emetic; dye with  $1\frac{1}{2}$  oz. New Methylene blue GG. (40) *Dark Violet*.—Mordant with 3 lb. tannic acid and 2 lb. tartar emetic, then dye with 4 lb. Fast neutral violet B. (41) *Bright Yellow*.—Mordant with 2 lb. tannic acid and 1 lb. tartar emetic, and dye with 2 lb. Thioflavine T. (42) *Primrose Yellow*.—Mordant with 1 lb. tannic acid and  $\frac{1}{4}$  lb. tartar emetic, and dye with 2 oz. Thioflavine T. (43) *Navy Blue*.—Mordant with 5 lb. sumac extract and 3 lb. copperas, then dye with 2 lb. New Methylene blue R. (44) *Violet*.—Mordant with 3 lb. tannic acid and 2 lb. tartar emetic, and dye with 2 lb. New Methylene blue 3R. (45) *Dark Blue*.—Mordant with 5 lb. sumac extract and 3 lb. copperas, and dye with 2 lb. New Methylene blue NX. (46) *Blue Black*.—Mordant with 8 lb. sumac extract and iron liquor, then dye with 3 lb. Metaphenylene blue B. (47) *Emerald Tint*.—Mordant the cotton in the usual way with 1 lb. tannic acid and 1 lb. tartar emetic; dye to shade at  $180^{\circ}$  F. in a bath containing 14 oz. Auramine G, 2 oz. Brilliant green, then lift, wash and dry. (48) *Orange*.—Mordant with 3 lb. tannic

acid and 2 lb. tartar emetic, then dye with 4 lb. Tannin orange R. (49) *Scarlet*.—Mordant with 3 lb. tannic acid and 2 lb. tartar emetic, and dye with 2 lb. Tannin orange R and 1 lb. Safranine S. (50) *Dark Scarlet*.—Mordant with 3 lb. tannic acid and 2 lb. tartar emetic, and dye with  $\frac{1}{2}$  lb. Tannin orange R and 2 lb. Safranine S. (51) The Janus colours are a series of dyes of a basic nature which can be applied somewhat differently to the ordinary basic dyes, although the ordinary method can be followed. With these Janus dyes a two-bath process is followed. A dye-bath is prepared containing the dyestuff, sulphuric acid and common salt, and this is used at the boil from half to three-quarters of an hour, and the goods are allowed to remain in another three-quarters of an hour while the bath cools down. Next the dyed goods are run in a fixing bath of sulphuric acid, tannic acid and tartar emetic, this is used at the boil from half to one hour, after which the dyed goods are taken out and washed. If necessary the goods may be now topped with basic colours in order to produce any desired shade. The following recipes will show how the Janus dyes may be used. (52) *Blue*.—Dye with 9 oz. sulphuric acid, 8 oz. Janus blue G and 5 lb. common salt; fix with  $\frac{3}{4}$  lb. sulphuric acid, 8 oz. tannic acid and 4 oz. tartar emetic. (53) *Turquoise Blue*.—Dye with 9 oz. sulphuric acid, 1 lb. Janus green B and 10 lb. salt, fixing with  $\frac{3}{4}$  lb. sulphuric acid, 1 lb. tannin and  $\frac{1}{2}$  lb. tartar emetic. (54) *Dark Blue*.—Dye with 9 oz. sulphuric acid,  $2\frac{1}{2}$  lb. Janus blue R and 15 lb. common salt; fix with  $\frac{3}{4}$  lb. sulphuric acid,  $2\frac{1}{2}$  lb. tannic acid and  $1\frac{1}{4}$  lb. tartar emetic. (55) *Buff*.—Dye with 9 oz. sulphuric acid, 2 oz. Janus yellow R and 3 lb. salt; fix with  $\frac{3}{4}$  lb. sulphuric acid, 3 oz. tannic acid and 3 lb. tartar emetic. (56) *Crimson*.—Dye with 9 oz. sulphuric acid,  $2\frac{1}{2}$  lb. Janus red B and 15 lb. salt, fixing with  $\frac{3}{4}$  lb. sulphuric acid,  $2\frac{1}{2}$  lb. tannic acid and  $1\frac{1}{4}$  lb. tartar emetic. (57) *Red Violet*.—Dye with 9 oz. sulphuric acid, 1 lb. Janus claret red B and

10 lb. salt ; fix with 12 oz. sulphuric acid, 1 lb. tannic acid and  $\frac{1}{2}$  lb. tartar emetic. (58) *Orange*.—Dye with 9 oz. sulphuric acid, 1 lb. Janus yellow R and 10 lb. salt ; fix with 12 oz. sulphuric acid, 1 lb. tannic acid and  $\frac{1}{2}$  lb. tartar emetic. (59) *Dark Violet*.—Dye with 9 oz. sulphuric acid, 2 lb. Janus grey B and 15 lb. salt ; fix with 12 oz. sulphuric acid,  $2\frac{1}{2}$  lb. tannic acid and  $1\frac{1}{4}$  lb. tartar emetic. (60) *Chocolate Brown*.—Dye with 9 oz. sulphuric acid,  $3\frac{1}{2}$  lb. Janus brwn B and 15 lb. salt, fixing with 2 oz. sulphuric acid,  $2\frac{1}{2}$  lb. tannic acid and 1 lb. tartar emetic.

#### 6. DYEING ON METALLIC MORDANTS.

There are a number of dyestuffs or colouring matters like alizarine, logwood, fustic, cutch, resorcin green, etc., which have no affinity for the cotton fibre, and of themselves will not dye it. They have the property of combining with metallic oxides such as those of iron, chromium, aluminium, tin, lead, calcium, etc., to form coloured bodies which are more or less insoluble in water. These coloured bodies are called "colour lakes," and the metallic compounds used in connection with their production "mordants," hence often the dyestuffs applied by this method are termed "mordant dyes." In the case of the natural dyestuffs—logwood, fustic, Persian berries, Brazil wood, camwood, cochineal, quercitron, cutch, etc.—which belong to this group of "mordant dyes," the whole of the material does not enter into the operation, but only a certain constituent contained therein, which is commonly soluble in boiling water, and extracted out by boiling. This constituent is called the "colouring principle" of the dyestuff, or wood, and naturally varies with each. It is not intended here to deal in detail with these colouring principles. The methods of applying and the colours which can be got from these dyes varies very

much. Roughly, the modes of application fall under three heads : (1) the particular metallic mordant is first fixed on the fibre by any suitable method, and then the fibre is dyed ; (2) the dyestuff is first applied to the fibre, and then the colour is fixed and developed by treatment with the mordant ; and (3) the dyestuff and the mordant are applied at the same time. This last method is not much used. In the following sections many examples of these methods will be given. The dyes fixed with metallic mordant vary in their composition and properties. There is first the group of eosine dyes, which are acid derivatives of a colour-base, and, in virtue of being so, will combine with the metallic oxides. The colour of these colour lakes depends not only on what oxide is used, but also on that of the particular eosine dye employed. Moreover the particular salt of the metallic oxide used also exerts an influence. The nitrate of lead gives brighter tones than the acetate. Then there are some members of the azo dyes, particularly the croceine scarlets, which can also be dyed on the cotton by the aid of tin, lead or alum mordants.

*Mordant Dyes.* - The most important class of dyestuffs which are dyed on to cotton with a metallic mordant is that to which the term "mordant dyes" is now given. This includes such dyes as logwood, fustic, madder, alizarine, and all the dyes derived from anthracene. Many of these are not really dyes, that is, they will not of themselves produce or develop a colour on to any fibre when used alone ; it is only when they combine with the mordant oxide which is used, and then the colour varies with the mordant. Thus, for instance, logwood with iron produces a bluish black ; with chrome, a blue ; with alumina, a reddish blue. Alizarine with iron produces a dark violet ; with alumina, a scarlet ; with chrome, a red ; with tin, a bright scarlet. Fustic gives, with tin and alumina, bright yellows ; with chrome, a dark

from alizarine blues ; greens from Coeruleine or Dinitroso-resorcine, etc. • Another method of mordanting cotton for the mordant group of dyestuffs is that in which the cotton is impregnated with a salt of the mordant oxide derived from a volatile acid such as acetic acid, and then subjected to heat or steaming. This method is largely taken advantage of by calico printers for grounds, and dyers might make use of it to a much larger extent than they do.

*Chemicals used in Mordanting Cotton.*—There are used in this process the acetates of iron, chromium and aluminium, and bisulphites of the same metals and a few other compounds. Baths of these are prepared, and the cotton is impregnated by steeping in the usual way ; then it is gently wrung out and aged, that is, hung up in a warm room overnight. During this time the mordant penetrates more thoroughly into the substance of the fabric, while the acid, being more or less volatile, passes off—probably not entirely, but at any rate some of the metal is left in the condition of oxide and the bulk of it as a basic salt. Instead of ageing the cotton may be subjected to a process of steaming with the same results. After this the cotton is ready for dyeing, which is done by the method described in the last section. There is still another method to be noticed here, that is, one in which a bath is prepared containing both the mordant and the dyestuff. In this case the character of the mordant must be such that, under the conditions that prevail, it will not form a colour lake with the dyestuff. Such substances are the bisulphites, if used with the bisulphite compounds of the dyestuffs ; the acetates, if mixed with some acetic acid, may also be used. The process consists in preparing the dye-bath containing both the mordant and the dyestuff, entering the cotton, steeping for some time, then wringing and steaming. During the latter operation the acid combined with the mordant, being volatile, passes away, and the colouring

matter and mordant enter into combination to form the colour lake, which is firmly fixed upon the fibre. Very good results may be obtained by this method. Lastly, in connection with the mordant colours, attention may be directed to the process of using some of them, which consists in making a solution of the dyestuff in ammonia, impregnating the cotton with this alkaline solution and subjecting it to a steaming operation, during which the alkali, being volatile, passes away, leaving the colouring matter behind in an insoluble form. The cotton is next passed into a weak bath of the mordant (preferably the acetates of iron, etc.), this being used first cold and then gradually heated up. The dye on the fibre and the mordant combine to form the desired colour, which is fixed on the fibre. The chrome mordants are those which are most commonly applied by the methods here sketched out, and with the large and increasing number of mordant dyes available, the processes should be worth attention from the cotton dyer.

The following recipes give fuller details than the outline sketches of the methods given above for the use of the various dyes produced with the mordant dyes and metallic mordants. In some cases, as will be seen, other dyes may be added to produce special shades. (1) *Dark Olive*.—Prepare a bath from 8 lb. cutch, 4 lb. logwood extract, 7 lb. fustic extract, 2 lb. copper sulphate. Work in this for one to one and a half hours at the boil. This bath may be kept standing, adding new ingredients from time to time, and works best when it gets old. Then pass into a cold bath of 3 lb. copperas for one hour, then wash and enter into a new bath of 10 lb. salt, 6 oz. Titan blue 3B, 6 oz. Titan brown R, 6 oz. Titan yellow Y, work for one hour at the boil, then lift, wash and dry. (2) *Brown*.—Prepare a bath with 20 lb. cutch, 2 lb. copper sulphate, 4 lb. quercitron extract. Work for one and a quarter hours at the boil, then allow to lie for a day, when the goods

are passed into a bath containing 3 lb. bichrome and 1 lb. alum. Work at 150° to 160° F. in this for a few minutes, then allow to lie for four to five hours, wash well and dry. (3) *Olive*.—Work for twenty minutes at 80° F. in a bath of 10 lb. fustic extract, 5 lb. quercitron extract, 2 lb. logwood extract ; heat to boil, work for half an hour, then enter in a cold bath of 2 lb. sodium bichromate<sup>1</sup> and 5 lb. copper sulphate ; work for twenty minutes, then heat to boil ; work for twenty minutes more, wash and dry. (4) *Pale Brown*.—Treat in a hot bath of 2½ lb. cutch, 1¾ lb. bluestone ; work for half an hour in this bath, then lift, wring and work in a bath of 1¾ lb. bichrome for twenty to thirty minutes. Dye in a bath of 2½ lb. alum, 7 oz. Chrysoidin, 14 oz. Ponceau B. (5) *Fast Brown*.—The cotton is heated in a boiling bath containing 20 lb. cutch, 4 oz. copper sulphate for one hour, it is then treated in a bath containing 8 oz. bichrome for half an hour, then dyed in a bath containing 2 oz. Benzo black blue, 6 oz. Benzo brown NB, 2 lb. soap, 8 lb. salt, for one hour at the boil, washed and dried. (6) *Drab*.—Dissolve ½ lb. cutch, 7 lb. bluestone, 8 lb. extract of fustic ; enter goods at 120° F., give six turns, lift and drain. Prepare a fresh bath containing 2 lb. copperas ; enter goods, give three turns, lift and enter fresh bath at 120°, containing 2 lb. bichrome, give four turns, drain, wash and dry. (7) *Coffee Brown*.—For one piece, wet out in hot water, run for half an hour upon a jigger in a bath of 6 lb. good cutch, take up and drain in a bath of 3 lb. black iron liquor ; drain, run again through each bath and rinse well. Prepare a fresh bath with Bismarck brown, enter at 100° F., heat slowly to 200° F., drain, rinse and dry. (8) *Dark Brown Olive*.—Prepare the dye-bath with 12 lb. cutch, 2 lb. bluestone, 2½ lb. alum, 10 lb. quercitron extract, 2 lb. indigo carmine, 4 lb. turmeric, ¼ lb. Bismarck brown ; boil for one and a half

<sup>1</sup> Note.—100 lb. pure sodium bichromate is equal to 104 lb. of bichromate of potash (bichrome).

hours, then lift and add 1 lb. copperas ; re-enter the goods, give another half-hour, boil, then add 1½ lb. bichrome, work two hours more, then wash and dry. (9) *Red Drab*.—Boil up 10 lb. cutch and 5 lb. sumac ; enter the cotton at 140° F., work fifteen minutes and lift. Prepare a fresh bath of 4 lb. black iron liquor ; enter the cotton cold, work ten minutes and lift. Prepare another bath with 3 lb. bichrome ; enter cotton at 160° F., work fifteen minutes, lift and wash. Finish in a fresh bath containing 3 lb. logwood, 6 lb. red liquor ; enter cotton at 100° F., work ten minutes, lift, wash and dry. (10) *Fawn*.—Boil up 5 lb. cutch and 5 oz. bluestone, cool to 100° F. ; enter, give six turns, lift, and add 2 lb. copperas ; re-enter cotton, give four turns, lift and wring. Prepare a fresh bath with 1 lb. bichrome ; enter cotton at 110° F., give five turns, lift, wash and dry. (11) *Grey Slate*.—Boil up 10 lb. sumac, 3 lb. fustic extract ; cool down to 120° F., give eight turns, lift and wring. Prepare a fresh bath with 5 lb. copperas ; enter cotton cold, give five turns, lift and wash. (12) *Dark Plum*.—Lay down overnight in 30 lb. sumac. Next morning wring and enter in a fresh bath of oxy-muriate of tin 20° Tw., give four turns, lift and wash well in two waters. Boil out 40 lb. ground logwood, 10 lb. ground fustic, cool bath down to 140° F. : enter cotton, give eight turns, lift and add 1½ gallons red liquor ; re-enter yarn, give four turns, lift, wash and dry. (13) *Pale Chamois*.—Work the cotton seven turns in a cold bath of 3 lb. copperas, then wring and pass into a cold bath of 3 lb. soda ash ; work well, wash and dry. (14) *Dark Brown Olive*.—Prepare a bath of 28 lb. fustic, ¾ lb. logwood, 18 lb. cutch, 4 lb. turneric, 2 lb. copper sulphate, ¾ lb. alum ; work for an hour at the boil, then sadden in a new bath of 1 lb. bichrome for half an hour, then sadden in a new bath of ¼ lb. pitrate of iron, working in the cold for half an hour ; lift, wash and dry. (15) *Havana Brown*.—Prepare a bath with 4 lb. cutch and 1 lb. bluestone ;

work at the boil for one hour, then pass through a warm bath of  $\frac{1}{2}$  lb. bichrome, 1 lb. sulphuric acid. Wash and dye in a bath of  $\frac{3}{4}$  lb. Bismarck brown and 4 lb. alum ; work for one hour at about  $180^{\circ}$  F., wash and dry. (16) *Black*.—Prepare a dye-bath with 20 lb. extract of logwood, 4 lb. cutch, 5 lb. soda ash, 5 lb. copper sulphate. Heat to the boil, enter the cotton, and work well for three hours, then lift, and allow to lie overnight in a wet condition, wash and pass into a bath of 1 lb. bichrome for half an hour ; lift, wash and dry. The dye-bath is not exhausted, and only about one-third of the various drugs need be added for further batches of cotton.

(17) *Reseda Green*.—Prepare a bath with 15 lb. cutch, 8 lb. turmeric : work in this for fifteen minutes at about  $150^{\circ}$  F., then pass through a hot bath of 2 lb. bichromate of potash for one hour, then re-enter into a cutch bath to which has been added 1 lb. sulphate of iron ; work for one hour, then add 2 lb. alum, and work half an hour longer ; rinse, wash and dry.

(18) *Fawn Brown*.—Prepare a dye-bath with 4 lb. cutch, 2 lb. fustic extract ; work for one hour at hand heat, then lift and pass through a bath of  $1\frac{1}{4}$  lb. bichromate of potash ; work for a quarter of an hour, rinse, and pass into a fresh bath of 1 oz. Bismarck brown for ten minutes, then lift, wash and dry.

(19) *Beige*.—Prepare a bath with 20 lb. sumac ; enter cotton at  $120^{\circ}$  F., give six turns, lift and add  $\frac{1}{2}$  lb. copperas ; re-enter cotton, give four turns, and wring. Prepare a fresh bath containing 2 lb. extract of fustic, 3 oz. extract of indigo ; enter cotton at  $120^{\circ}$  F., give three turns, raise temperature to  $140^{\circ}$  F., and turn to shade ; lift, wash and dry. (20) *Turkey Red*.

—One of the most important colours dyed on cotton is that known as Turkey red, a bright red of a bluish tone, characterised by its great fastness to light washing, etc. Strong alkalis turn it more yellowish, but weak acids and alkalis have little action. Into the history of the dyeing of Turkey red it is not intended to enter, those who are interested in the

subject should refer to old works on dyeing ; nor is it intended to speak of old methods of producing it with the aid of madder, but rather to give some of the most modern methods for dyeing it with alizarine. Many processes, differing somewhat in detail, have been devised for dyeing Turkey red on cotton, and it is probable that no two Turkey red dyers work exactly alike. It is difficult to produce the most perfect red, and a very great deal of care in carrying out the various operations is necessary to obtain it. This care and the number of operations makes Turkey red an expensive colour to dye, and so shorter methods are in use which dye a red on cotton that is cheaper, but not so brilliant or fast as a true Turkey red.

*Process A.*--This process is perhaps the most elaborate of all processes, but it yields a fine red. The process is applicable to cloth or yarn, although naturally the machinery used will vary to suit the different conditions of the material. Bleached yarn or cloth may be treated, although a full bleach is not necessary, but the cloth or yarn must be clean or well scoured, so that it is free from grease and other impurities. (1) Boil the cotton for six to eight hours with a carbonate of soda lye at 1° Tw. in a keir at ordinary pressure, then wash well, wring, or, better, hydro-extract. (2) *First "greening"* : What is called the "first green liquor" is prepared by taking 15 lb. of gallipoli oil, 3 1/2 lb. phosphate of soda and 15 lb. carbonate of soda, the liquor to stand at 2° Tw. Originally this "liquor" was made with sheep dung, but this is now omitted. The cotton is worked in this liquor, which is kept at 100° F., until it is thoroughly impregnated, then it is taken out, squeezed and dried, or in some cases piled overnight and then stoved. (3) *Second green liquor* : As before. (4) *Third green liquor* : As before. (5) *white liquor treatment* : A carbonate of soda liquor of 2° Tw. strength is prepared, and the cotton steeped in this until it is thoroughly impregnated,

then it is wrung out and stoved. (6) *Second white liquor* : As before. (7) *Sleeping* : Prepare a bath of water at 150° F., and steep for twelve hours, then wring and dry. (8) *Sumac-ing* : A liquor is made from 12 lb. sumac with water, and after straining from undissolved sumac leaves the liquor is made to stand at 2° Tw.; this is kept at about 100° F., and the cotton is well worked in it and allowed to steep for four hours, after which it is taken out and wrung. (9). *Mordant-ing or aluming* : 20 lb. of alum are dissolved in hot water, and 5 lb. of soda crystals are slowly added in order to prepare a basic alum solution; this is now made by the addition of water to stand at 8° (sp. gr. 1.040) Tw. The sumac-treated cotton is worked in this bath and allowed to steep for twenty-four hours, when it is taken out and wrung. Some dyers add a little tin crystals to this bath; others add a small quantity of red liquor. (10) *The dyeing* : A cold bath is prepared with 10 lb. to 12 lb. alizarine, 3 lb. sumac extract and 2 oz. lime. The cotton is entered into the cold bath, worked from fifteen to twenty minutes so as to get it thoroughly impregnated; then the heat is slowly raised to the boil and the dyeing carried on at that heat until the full shade is obtained, which usually takes about an hour. According to the brand of alizarine used so will the shade that is obtained vary, as will be mentioned later on. (11) *First clearing* : The dyed cotton is placed in a boiler and boiled for four hours with 3 lb. soda crystals and 3 lb. palm oil soap, afterwards washing well. (12) *Secon'l clearing* : The dyed cotton is again boiled for two hours with 2½ lb. soap and ½ lb. tin crystals, then give a good washing and dry. This process is a long one—indeed, some dyers by repeating some of the operations lengthen it—and it takes at least two weeks; in some case three weeks, to carry out. The idea is to get the cotton first thoroughly impregnated with the oil, and this oxidised to some extent on the fibre, and to this end the oil treatments are carried

out. In this process experience has shown that olive oil is the best to use, although other oils have been tried from time to time. The sumacing enables the alumina to be more firmly fixed on to the cotton. The alumina combines with both the oil and the sumac, and the resulting mordant produces a better and more brilliant red with the alizarine. The clearing operations serve to remove impurities, to brighten the colour, and to more fully fix it on the cotton.

*Process B.*—(1) *Bleaching* : The cotton is well bleached or scoured with soda in the usual way. (2) *Oiling or preparing* : A liquor is made from 10 lb. alizarine oil or Turkey red oil in 10 gallons water. This oil is prepared from castor oil by a process of treatment with sulphuric acid, washing with water and neutralising with caustic soda. The cotton is thoroughly impregnated with this oil by steeping, then it is wrung out and dried. (3) *Steaming* : The cotton is put into a steaming cottage or continuous steaming chamber and steamed for from one to one and a half hours at about 5 lb. pressure. (4) *Fixing bath* : A bath of red liquor (acetate of alumina) at  $8^{\circ}$  Tw. is prepared. Some dyers use basic alum at the same strength. In this bath the cotton is steeped at  $100^{\circ}$  F. for two hours ; then it is wrung out and dried. This alumming bath can be repeated. Next it is run through a bath of chalk and water containing 2 lb. chalk in 10 gallons water. This helps to fix the alumina on the cotton. Phosphate of soda also makes a good fixing agent. (5) *Dyeing* : This is carried out in precisely the same way as in the other process. (6) *Oiling* : A second oiling is now given in a bath of 5 lb. alizarine oil, or Turkey-red oil, in 10 gallons water, after which the cotton is dried, when it is ready for further treatment. In place of giving a second oiling after the dyeing, it is, perhaps, better to give it after the mordanting and before dyeing. (7) *Clearing* : The dyed cotton is cleared with soap in the same manner as the clearing operations of the

first process, which see. Any of the treatments preparatory to, and following the actual dyeing of, any of these processes may be repeated if deemed necessary. The text-books on dyeing and the technical journals devoted to the subject frequently contain accounts of methods of dyeing Turkey red, but when these come to be dissected the methods are but little more than variants of those which have just been given. Seeing that the theory or theories involved in this rather complex process of dyeing Turkey red, and that colourists are not agreed as to the real part played by the oil, the sumac and the clearing operations in the formation of a Turkey red on cotton, nothing will be said here as to the theory of Turkey-red dyeing.

*Alizarine Red.*—It is possible to dye a red with alizarine on cotton which, while being a good colour, is not quite so fast to washing, etc., as a Turkey red. This is done by using fewer treatments, as shown in the following process :—

- 1.—Boil the cotton in soda.
- 2.—Oil with Turkey-red oil, as in the Turkey-red process No. 2 above.
- 3.—Mordant with alum or acetate of alumina.
- 4.—Dye with alizarine as before.
- 5.—Soap.

There are three distinct colouring-matters which are sold commercially under the name of "alizarine." These are alizarine itself, which produces a bluish shade of red; anthra-purpurine, which gives a similar but less blue red than alizarine; and flavo-purpurine, which produces the yellowest reds. The makers send out all these various products under various marks.

For dyeing Turkeyreds the flavo- and anthra-purpurine brands or yellow alizarines are to be preferred; for pinks and rose shades the alizarine or blue shade brands are best.

*Alizarine Pink.*—This can be dyed in the same way as Turkey red, only using for full pinks 4 per cent. of alizarine in the dye-bath, or for pale pinks 1 to 2 per cent. It is advisable to reduce the strength of the oiling and mordanting baths down to one-half.

*Alizarine Violet.*—Alizarine has the property of combining with iron to form a dark violet colour, and advantage is taken of this fact to dye what are called in the dyeing and calico printing trades alizarine purples and lilacs, although these do not resemble in hue or brilliance the purples and lilacs which can be got from the direct dyes. They have not the importance which they formerly possessed, and but a mere outline of two processes for their production will be given.

*Alizarine Purple.*—1. (1) Boil with soda. (2) Prepare with Turkey red oil. (3)

Mordant by steeping in copperas liquor at 4° Tw. for twenty minutes, take out, allow to lie on stillages overnight, then wash and dry. For deep purples it may be advisable to repeat these treatments; for pale lilacs using them at half strength is advisable. (4) Dye with 8 to 10 per cent. of alizarine blue shade, working as described under Turkey red.

The best results are obtained when 1 per cent. of chalk is added to the dye-bath. (5) Soap as in red dyeing. 2.

(1) Boil with soda. (2) Oil with Turkey red oil. (3) Steep pyrolignite of iron (iron liquor) for one hour, then age by hanging in the air. (4) Dye as before. (5) Soap. Fine blacks are got if after oiling the cotton is treated with sumac or tannic acid, then mordanted with iron and dyed with alizarine as usual.

(1) *Chocolate Browns.*—Fine fast chocolate browns can be got from alizarine by using a mixed mordant of iron and alumina, either the acetate or the sulphate. By varying the relative proportions various shades can be obtained. (2) *Alizarine Orange.*—Prepare the cotton as if for dyeing a Turkey red, but use in the dye-bath 8 to 10 per cent. of alizarine orange. (3) *Alizarine Blue.*—The

cotton is boiled three hours with 3 per cent. ammonia soda at 30 lb. pressure, and then washed thoroughly. The boiled, washed and hydro-extracted yarn is oiled with a solution containing from  $\frac{1}{4}$  lb. to  $1\frac{1}{2}$  lb. Turkey red oil, 50 per cent. for every gallon of water. It is then wrung out evenly and dried for twelve hours at  $150^{\circ}$  F. *Tannin Grounding* : The oiled and dried cotton is worked three-quarters of an hour in a vat containing a tannin solution (1 oz. per gallon). The cotton remains in this liquid, which is allowed to cool off for twelve hours, then it is hydro-extracted. Sumac turns the shade somewhat greener, which is noticed especially after bleaching, therefore tannin is given the preference. *Chromium Mordant* : The cotton treated with tannin and then hydro-extracted is worked cold for one hour in a vat containing a solution of chromium chloride at  $32^{\circ}$  Tw., and remains in this solution twelve hours. The cotton is then hydro-extracted and washed directly ; it is best to employ running water. A special fixation does not take place. The cotton is now ready for dyeing. The solution of chromium chloride and the tannin solution can be used continuously, adding fresh liquor to keep the baths up to strength. *Dyeing* : For dyeing, water free from lime must be used. Water having not more than  $2\cdot5^{\circ}$  hardness can be employed if it is corrected with acetic acid, thereby converting the carbonate of lime into acetate of lime. Very calcareous water must be freed from lime before use. The dye-bath contains for 100 lb. cotton 15 lb. Alizarine blue paste (AR or F, according to the shade desired), 35 lb. acetic acid ( $12^{\circ}$  Tw.),  $15\frac{1}{2}$  lb. ammonia (25 per cent.),  $2\frac{1}{4}$  oz. tannin. The cotton is worked a quarter of an hour in the cold ; the temperature is raised slowly to a boil, taking about one hour, and the cotton is worked three-quarters of an hour at that heat. Finally, the cotton is washed and hydro-extracted. The dyed and washed cotton is steamed two hours at 15 lb. to 22 lb. pressure.

Steaming turns the shade greener and darker, and increases the fastness. After steaming the cotton it is soaped one or two hours at the boil, with or without pressure. According to the quality of water employed, 2 to 5 parts soap per 1000 parts water are taken. (4) *Brown*.—A fine brown is got by a similar process to this, if instead of Alizarine blue, Alizarine orange is used in the dye-bath. A deeper brown still if Anthracene brown, or a mixture of Anthracene brown and Alizarine blue, be used. (5) *Claret Red*.—Clarets to maroon shade of red are obtained by preparing the cotton as for blue given above, then dyeing with alizarine.

#### LOGWOOD BLACK.

The formation of logwood black on the fibre depends upon the fact that the colouring principle of logwood forms a black colour lake with iron and also one with chromium. There are many ways of dyeing logwood blacks on cotton, whether that be in form of hanks of yarns, warps or pieces. While these blacks may be, and in the case of hanks are, dyed by what may be termed an intermittent process, yet for warps and piece goods a continuous process is preferred by dyers. Examples of both methods will be given. As in the dyeing of Turkey reds, it is probable that no two dyers of logwood blacks quite agree in the details of their process, there may be variations in the order of the various baths and their relative strengths. Typical methods will be noted here.

• **Dyeing Logwood Black on Yarn in Hanks.**—(1) *Sumacing*: Prepare a bath with 10 lb. sumac extract in hot water. Work the yarn in this for half an hour, then allow to steep for six hours or overnight, lift and wring. The liquor which is left may be used again for another lot of yarn by adding 5 lb. sumac extract for each successive lot of yarn. In place of

using sumac the cheaper myrabolam extract may be used.

(2) *Ironing or saddening* : Prepare a bath with  $3\frac{1}{2}$  gallons nitrate of iron,  $80^{\circ}$  Tw. Work the yarn in this for fifteen minutes, then wring out. The bath may be used again when 1 gallon of nitrate of iron is added for each lot of yarn worked in it. In place of the nitrate of iron, the pyrolignite of iron or iron liquor may be used. (3) *Liming* : Work for ten minutes in a weak bath of milk of lime. (4) *Dyeing* : This is done in a bath made from 10 lb. logwood extract and 1 lb. fustic extract. The yarn is entered into the cold or tepid bath, the heat slowly raised to about  $150^{\circ}$  F., then kept at this heat until a good black is got, when the yarn is taken out, rinsed and wrung. The addition of the fustic extract enables a much deeper and jetter shade of black to be dyed.

(5) *Saddening* : To obtain a fuller black the dyed cotton is sent through a bath of  $1\frac{1}{2}$  lb. copperas, then washed well.

(6) *Soaping* : Work for twenty minutes in a bath of 2 lb. soap at  $140^{\circ}$  to  $150^{\circ}$  F. Then wash well. Much the same process may be followed for dyeing logwood black on warps and piece goods, jiggers being used for each operation. Another method is to first work the cotton in pyrolignite (iron liquor) at  $10^{\circ}$  Tw., until it is thoroughly impregnated, then to dry and hang in the air for some hours, next to pass through lime water to fix the iron, and then to dye as before.

*Continuous process* : In this case a continuous dyeing machine is provided, fitted with five to six compartments. The cotton is first of all prepared by steeping in a bath of 12 lb. myrabolam extract for several hours, then it is taken to the continuous machine and run in succession through nitrate of iron liquor, lime water, logwood and fustic, iron liquor and water. The nitrate of iron bath contains 2 gallons of the nitrate to 10 gallons of water, and as the pieces go through fresh additions of this liquor are made from time to time to keep up the volume and strength of the liquor to the original points. The

logwood bath is made from 10 lb. logwood extract and 1 lb. fustic extract, and it is used at about 160° F. The quantities here given will serve for 100 lb. of cotton, and it is well to add them dissolved up in hot water in small quantities from time to time as the cotton goes through the bath. The iron liquor given after the dyeing contains 2 lb. of copperas in 10 gallons of water. Between the various compartments of the machine is fitted squeezing rollers to press out any surplus liquor, which is run back into the compartment. The rate of running the warp or pieces through should not be too rapid, and the dyer must adapt the rate to the speed with which the cloth dyes up in the dye-bath. The addition of a little red liquor (alumina acetate) to the iron bath is sometimes made : this is advantageous, as it results in the production of a finer black. Iron by itself tends to give a rusty-looking or brownish black, but the violet, or lilac shade that alumina gives with logwood, tones the black and makes it look more pleasant. Some dyers add a small quantity, 1 per cent., of the weight of the cotton of sulphate of copper to the iron bath, others add even more than this. Some use nitrate of copper ; the copper giving a greenish shade of black with logwood, and this tones down the iron black and makes it more gloomy in appearance. Single bath methods of dyeing logwood blacks are in use ; such methods are not economical, as a large quantity, both of dye-wood and mordants, remains in the bath unused. Although full intense blacks can be dyed with them, the black is rather loosely fixed and tends to rub off. This is because as both the dyestuff and the mordant are in the same bath together they tend to enter into combination and form a colour lake that precipitates out in the dye-bath, causing the loss of material alluded to above, while some of it gets mechanically fixed on the cotton, in a more or less loose form, and this looseness causes the colour to rub off. For a *chrome-logwood black*, a dye-bath is made

with 3 lb. bichromate of potash, 100 gallons logwood decoction at  $3^{\circ}$  Tw. and  $6\frac{1}{2}$  lb. hydrochloric acid. Enter the cotton into the cold bath, raise slowly to the boil and work until the cotton has acquired a full black blue colour, then take it out and rinse in a hot lime water when a blue black will be got. A *copper logwood black* is got by taking 100 gallons logwood decoction at  $3^{\circ}$  Tw. and 6 lb. copper acetate (verdigris); the cotton is entered cold and brought up to the boil. Copper nitrate may be used in the place of the copper acetate, when it is a good plan to add a little soda to the bath. Some dyers in working a copper-logwood black make the dye-bath from 100 gallons logwood liquor at  $2^{\circ}$  Tw., 4 lb. copper sulphate (bluestone) and 4 lb. soda. This bath is used at about  $180^{\circ}$  to  $190^{\circ}$  F., for three-quarters of an hour, then the cotton is lifted out, wrung and aged, or, as it is sometimes called, "smothered" for five hours. The operations are repeated two or three times to develop a full black. Logwood black dyeing lost much of its importance of late years owing to the introduction of the many direct blacks, which are much easier of application and leave the cotton with a fuller and softer feel. *Logwood Greys*.—These are much dyed on cotton and are nothing more than weak logwood blacks, and may be dyed by the same processes only using baths of about one-tenth the strength. By a one-bath process 5 lb. of logwood are made into a decoction and to this 1 lb. of copperas (ferrous sulphate) is added and the cotton is dyed at about  $150^{\circ}$  F. in this bath. By adding to the dye-bath small quantities of other dye-woods, fustic, peach wood, sumach, etc., greys of various shades are obtained. Some recipes bearing on this point are given in this section. Logwood is not only used for dyeing blacks and greys as the principal colouring matter, but is also used as a shading colour along with cutch, fustic, quercitron, etc., in dyeing olives, browns, etc., and among the recipes given in this section examples of its use in this direc-

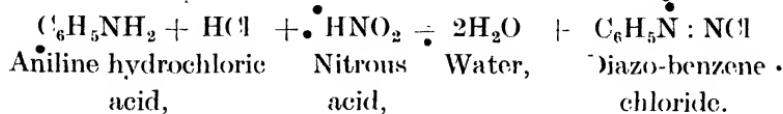
tion will be found. The dye-woods—fustic, Brazil wood, barwood, Lima wood, camwood, cutch, peach wood, quercitron bark, Persian berries—since the introduction of the direct dyes lost much of their importance and were little used, but recent events have also created a re-demand for all natural dyestuffs. Cutch is used in the dyeing of browns and several recipes have already been given. Their production consists essentially in treating the cotton in a bath of cutch, either alone or for the purpose of shading with other dye-woods when the cotton takes up the tannin and colouring matter of the cutch, etc. The colour is then developed by treatment with bichromate of potash, either with or without the addition of an iron salt to darken the shade of brown. The usual methods of applying all the other dye-woods, to obtain scarlets to reds with Brazil wood, Lima wood, peach wood; or yellows with fustic, quercitron or Persian berries, is to first prepare the cotton with sumac, then mordant with alumina acetate or tin crystals (the latter gives the brightest shades), then dye in a decoction of the dye-woods. Sometimes the cotton is boiled in a bath of the wood when it takes up some of the dye-wood, next there is added alumina acetate or tin crystals and the dyeing is continued when the colour becomes developed and fixed upon the cotton. Iron may be used as a mordant for any of these dye-woods, but it gives dull sad shades. Chrome mordants can also be used and these produce darker shades than tin or alumina mordants. As practically all these dye-woods are now not used by themselves it has not been deemed necessary to give specific recipes for their application, on previous pages several are given showing their use in combination with other dyes. The dyestuff Dinitroso-resorcine or Solid green O is used along with iron mordants for producing fast greens and with chrome mordants for producing browns to a limited extent in cotton dyeing. The following recipes give the

details of the process. (1) *Green*.—Steep the cotton yarn or cloth in the following liquor until well impregnated, then dry : 3 gallons iron liquor (pyrolignite of iron), 22° Tw. gallons of water,  $\frac{3}{4}$  gallon acetic acid, 12° Tw., 2 lb. ammonium chloride. Then pass the cotton through a warm bath of 3 oz. phosphate of soda and 4 oz. chalk per gallon, then enter into a dye-bath containing 6 lb. Solid green O. Work as described for dyeing alizarine red. For darker greens of a Russian green shade use 10 lb. of Solid green O in the dye-bath. (2) *Brown*.—A fine brown is got by steeping the cotton in a bath of 8 lb. Solid green O,  $6\frac{3}{4}$  gallons water,  $1\frac{1}{2}$  gallons ammonia and 2 lb. acetate of chrome ; dry, then pass through a soap-bath, wash and dry. (3) *Deep Olive Brown*.—Mix 8 lb. Solid green O and  $4\frac{1}{2}$  lb. borax with 6 gallons water, add  $\frac{1}{2}$  lb. Turkey-red oil, 5 lb. ammonia, then 2 gallons water and  $1\frac{1}{2}$  lb. copper-soda solution and another 2 gallons water. Steep the cotton in this, dry, soap well and wash. The copper-soda solution is made from 10 lb. chloride of copper (75° Tw.), 5 lb. tartaric acid, 12 lb. caustic soda (75° Tw.) and 4 lb. glycerine. (4) *Khaki*.—Make the dye-liquor from 14 lb. Solid green O,  $\frac{1}{2}$  lb. Alizarine yellow N, 1 lb. caustic soda (36° Tw.),  $\frac{1}{2}$  lb. Turkey-red oil and 8 gallons water. To this add  $2\frac{1}{2}$  lb. acetate of chrome (32° Tw.),  $2\frac{1}{4}$  lb. copper-soda solution and 4 gallons water. (5) *Sage Green*.—Use  $1\frac{1}{4}$  lb. Solid green O, 3 lb. caustic soda (36° Tw.),  $\frac{1}{2}$  lb. Ceruleine,  $\frac{1}{2}$  lb. Turkey-red oil, 1 gallon water to which is added  $2\frac{1}{2}$  lb. acetate of chrome (32° Tw.) and  $2\frac{1}{4}$  lb. copper-soda solution dissolved in 4 gallons water. (6) *Pale Brown*.—Use 4 lb. Solid green O,  $2\frac{1}{2}$  lb. borax, 3 lb. ammonia,  $\frac{1}{2}$  lb. Turkey-red oil, 6 gallons water and  $1\frac{1}{2}$  lb. copper-soda solution dissolved in 2 gallons water. (7) *Pale Fawn Brown*.—The dye-bath is made from  $\frac{1}{2}$  lb. Alizarine,  $1\frac{1}{4}$  lb. Solid green O,  $1\frac{1}{2}$  lb. borax,  $\frac{1}{2}$  lb. Turkey-red oil and 5 gallons of water to which is added  $1\frac{1}{2}$  lb. acetate of chrome (32° Tw.),  $1\frac{1}{2}$  lb. copper-soda solu-

tion and 4 gallons water. In all cases the cotton is steeped in the dye-liquors until thoroughly impregnated, then the excess liquor is wrung out, the cotton dried, then passed through a soap bath, washed well and dried. (8) *Dark Brown*.—Place the cotton in a lukewarm bath of 25 lb. cutch and  $1\frac{1}{2}$  lb. copper sulphate; work for half an hour, then steep for six hours, then lift, wring and enter into a bath of  $3\frac{1}{4}$  lb. bichromate of potash at  $160^{\circ}$  F. for twenty minutes. Then wash and dry. (9) *Yellow Brown*.—Make a bath with 14 lb. cutch and  $\frac{1}{2}$  lb. copper sulphate; work in this bath for four hours at  $120^{\circ}$  F., then pass into a bath of 2 lb. copperas and  $\frac{1}{2}$  lb. chalk, work for half an hour in the cold, then pass into a hot bath of  $2\frac{1}{2}$  lb. bichromate of potash at  $150^{\circ}$  F. for half an hour. (10) *Dark Brown*.—Make a dye-bath with 15 lb. cutch, 2 lb. logwood extract and 2 lb. fustic extract; work the cotton in this at  $160^{\circ}$  F. for three hours, then pass into a cold bath of 1 lb. copperas and  $\frac{1}{4}$  lb. chalk for half an hour, then into a bath of 3 lb. bichromate of potash for half an hour at  $150^{\circ}$  F., then wash and dry.

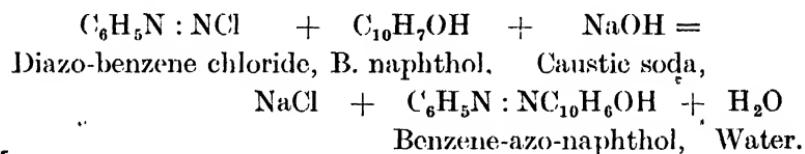
## 7. PRODUCTION OF COLOUR DIRECT UPON COTTON FIBRES.

By the action of nitrous acid upon the salts of the primary organic amines the so-called diazo compounds are formed. An example of this important process is that of nitrous acid on aniline hydrochloride shown in the following equation :—

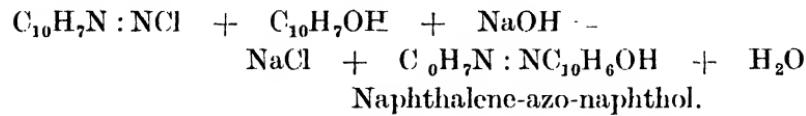


These diazo compounds are distinguished by their active properties, especially in combining with amines in acid solutions, or with phenols in alkaline solution to form the azo

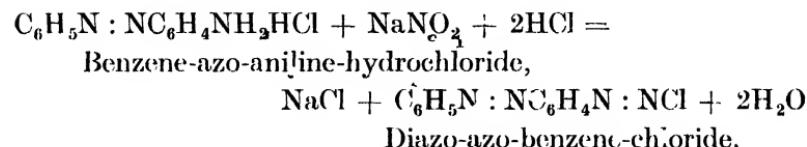
form are mixed with the requisite amount of nitrite, and the diluted paste then poured into the hydrochloric acid. It has been found by experience that the colour is developed much brighter upon the fibre when the diazo solution contains acetic acid and no free mineral acid. However, the diazotisation is better carried out with hydrochloric acid, and the presence of the latter is necessary to give stability to the solution. If before the diazo solution is used a quantity of acetate of soda be added to it, the free hydrochloric acid liberates acetic acid from the acetate, and the chloride of the diazo body changes into its acetate. It is better to add an excess above the two molecules of acetate of soda which are required. The combination when aniline and beta-naphthol are used, as the amine and phenol respectively, is shown in the following equations :—



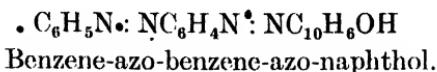
Or, with naphthylamine and naphthol, thus :—



By the action of nitrous acid upon amino-azo bodies a group of bodies called diazo-azo compounds are obtained which contain two N : N groups thus :—



When this compound is combined with naphthol diazo-azo dyes are produced.



The molecular weights of the bases, phenols and chemicals employed are the following : (1) Hydrochloric acid, HCl = 36.5. (2) Caustic soda, NaOH = 40. (3) Nitrite of soda, NaNO<sub>2</sub> = 69. (4) Acetate of soda, NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>·3H<sub>2</sub>O = 136.

1. Commercial hydrochloric acid at 32° Tw., specific gravity 1.160, contains about 365 grams of HCl (dry hydrochloric acid gas) in a litre, or 3½ lb. in a gallon.

2. The commercial 77 per cent. soda must always be used, and for practical purposes it may be taken as pure. It is best to make a solution which contains 160 grams NaOH in a litre of water (say, 10 lb. in 6 gallons<sup>1</sup>).

3. The nitrite supplied is almost chemically pure, and is easily soluble in water. In order to make a solution, 140 or 290 grams are dissolved per litre (say, 29 oz. to 100 oz.).

4. Crystallised acetate of soda contains 3 molecules of water of crystallisation, and is usually somewhat moist. Instead of 136 grams, 140 are taken to allow for moisture. The amount is dissolved in about 500 cubic centimetres of water.

*Bases.*—(1) Aniline, •C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> = 93. (2) Toluidine, C<sub>7</sub>H<sub>7</sub>NH<sub>2</sub> = 107. (3) Alpha- and beta-naphthylamine, C<sub>10</sub>H<sub>7</sub>NH<sub>2</sub> = 143. (4) Para- or meta-nitroaniline, C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>NH<sub>2</sub> = 138. (5) Nitro-para-toluidine, C<sub>7</sub>H<sub>6</sub>NO<sub>2</sub>NH<sub>2</sub> = 152. (6) Amidoazobenzene (base), C<sub>6</sub>H<sub>5</sub>N : NC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> = 197. (7) Orthoamidoazotoluol (base), C<sub>7</sub>HN : NC<sub>7</sub>H<sub>6</sub>NH<sub>2</sub> = 225. (8) Alpha- or beta-naphthol, C<sub>10</sub>H<sub>7</sub>OH = 144.

*Example of Quantities Taken.*—(1) Molecule nitrate, 69

<sup>1</sup> Note by Reviser.—10 lb. in a gallon of the finished fluid is quite a different proportion to 10 lb. to a gallon.

grams. (2) Molecule aniline, 93 grams. (3) Molecule hydro-chloric acid; 36.5 grams. (4) Molecule acetate of soda, 136 grams. (5) Molecule of naphthol, 144 grams. (6) Molecule of caustic soda, 40 grams. Applying the principles which have just been described to the dyeing of cotton, it is found that the cotton may be dyed by taking the base and preparing the diazo body, impregnating the cotton with this, and developing the colour by passing into a bath of the phenol. On the other hand, the cotton can be prepared with the phenol and the colour developed by passing into a bath of the diazotised base, and practice has shown that this latter proceeding is the best. Practically the only phenol that is used is the beta-naphthol ; alpha-naphthol is occasionally used, but not often. The purer the beta-naphthol the better, especially for producing the paranitroaniline red. Various preparations of beta-naphthol have been brought out by colour makers. The process of dyeing cotton with a naphthol colour takes place in two stages, the first being the grounding or preparing with the naphthol, the second the developing with the diazotised base. Some of the effects which can be obtained from the two naphthols and various bases are given in the following table :—

Base.	With beta-naphthol, gives	With alpha-naphthol, gives
1. Aniline,	Orange yellow ;	Cutch brown.
2. Paratoluidine,	Full yellow orange ;	" "
3. Metanitroaniline,	Fiery yellowish red ;	Brownish orange.
4. Paranitroaniline,	Bright scarlet ;	" "
5. Nitroparacetoluidine, <sup>n</sup>	Orange ;	Very bright catechu.
6. Alpha-naphthylamine,	Bluish claret red ;	Reddish puce.
7. Beta-naphthylamine,	Turkey red ;	
8. Aminoazobenzene.	Red ;	
9. Orthoaminoazotoluene,	Yellowish claret red ;	

By mixing alpha- and beta-naphthols together a variety of grenat and claret reds and browns can be obtained. With regard to the fastness of the shade produced the following may be considered :—

*Fast to Soaping.*

## Combination of A-Naphthol with Toluidine.

„	„	A-Naphthylamine.
„	„	B-Naphthylamine.
„	„	Amidoazobenzene.
„	B-Naphthol with Toluidine.	
„	„	Paranitroaniline.
„	„	Nitroparatoluidine.
„	„	B-Naphthylamine.
„	„	A-Naphthylamine.

*Moderately Fast.*

## Combination of A-Naphthol with Aniline.

„	„	Paranitroaniline.
„	„	Orthoamidoazotoluene.
„	B-Naphthol with Metanitroaniline.	
„	„	Amidoazobenzene.

*Very Loose.*

## Combination of A-Naphthol with Paratoluidine.

„	„	Metanitroaniline.
„	„	Nitroparatoluidine.
„	B-Naphthol with Aniline.	
„	„	Paratoluidine.
„	„	Orthoamidoazotoluene.

The samples were tested for fastness to light by exposing them for nine days with the following results :—

*Fast.*

Combination of A-Naphthol with (1) Aniline. (2) Toluidine. (3) Metanitroaniline. (4) Paranitroaniline. (5) Nitroparatoluidine. (6) B-Naphthylamine. (7) Aminoazobenzol. (8) Orthoaminoazotoluol.

*B-Naphthol with* (1) Aniline. (2) Paratoluidine. (3) Meta-nitroaniline. (4) Paranitroaniline. (5) B-Naphthylamine. (6) A-Naphthylamine.

*Moderately Fast.*

*Combination of B-Naphthol with Nitroparitoluidine.*

*Very loose.*

*Combination of A-Naphthol with* (1) Toluidine. (2) A-Naphthylamine.

*B-Naphthol with* (1) Toluidine. (2) Amidoazobenzene. (3) Orthoamidoazotoluene.

The most important of the naphthol colours is undoubtedly paranitroaniline red, produced by the combination of paranitroaniline and beta-naphthol. In order to produce the best and brightest shades these two bodies must be quite pure. The following directions may be followed.

**Dyeing Paranitroaniline Red on Yarn.**—It unfortunately happens that this red does not admit of being worked in large quantities at a time, particularly in the diazo bath where the colour is developed, as the previous operations seem to render the yarn slightly waterproof, and hence if large quantities of yarn were dealt with at one time some would be found to be dyed all right, others would be defective. It has, therefore, been found best to work only about 2 lb. of yarn at a time, carefully carrying out each operation with this quantity. As, however, the process can be quickly worked it follows that in the course of a day a fairly large quantity of yarn can be treated. (1) *Grounding*: The grounding or preparing bath for 100 lb. of yarn is best made in the following manner: 4 lb. of beta-naphthol are stirred in 2½ lb. of caustic soda liquor 70° Tw., then 1½ quarts of boiling water is added, when dissolved 1½ quarts of cold water. In a separate vessel dissolve

5 lb. Turkey-red oil in 11 quarts of water, then mix the two liquors together and add sufficient water to make up the whole to 12 gallons. In working sufficient of this liquor is taken and put into a deep tub in which 2 lb. of yarn can be conveniently worked. It is best to work at a tepid heat, say, 100° to 110° F.; 2 lb. of the yarn are worked in this liquor, so that it becomes thoroughly impregnated, then it is gently wrung out and hung up. This operation is repeated with each 2 lb. until the whole 100 lb. has been treated, adding from time to time some of the naphthol liquor to make up for that taken up by the cotton. When all the yarn has been through the liquor, give it another dip through the same liquor. Place the yarn in a hydro-extractor for five to seven minutes. Next open out the yarn well, and hang on sticks and dry in a stove at 140° to 150° F. The stove should be heated with iron pipes, through which steam at 30 lb. to 40 lb. pressure passes. The stove should be reserved entirely for this work, for if other goods be dried in it along with the naphthol-prepared cotton, any steam or acid vapours which might be given off from the former might damage the latter. When thoroughly dry the yarn is ready for the next operation.

(2) *Developing*: The developing bath is made in the following manner: 1½ lb. paranitroaniline is mixed with 1½ gallons of boiling water, and 1¾ quarts of hydrochloric acid at 30° to 32° Tw. Stir well until the paranitroaniline is completely dissolved, add 3½ gallons of cold water, which will cause a precipitation of the hydrochloride of paranitroaniline as a yellow powder. Let the mixture thoroughly cool off, best by allowing to stand all night; 1¼ lb. of nitrite of soda is dissolved in 4 quarts of cold water, and this solution is added to the paranitroaniline solution slowly and with constant stirring; in about fifteen to twenty minutes the diazotisation will be complete. At this and following stages the temperature of working should be kept as low as possible.

Some dyers use ice in preparing their diazo solutions, and certainly the best results are attained thereby, but with para-nitroaniline the ice can be dispensed with. After the end of the time sufficient cold water is added to bring the volume of the liquor up to 10 gallons. This diazo liquor will keep for some days, but it decomposes in time, so that it should not be kept too long. Another liquor is made by dissolving 4 lb. acetate of soda in 11 quarts of water. The developing bath is made by taking 4 gallons of the diazo liquor and 1 gallon of the acetate liquor and mixing together, and in this bath the prepared yarn, 2 lb. at a time, is worked. The colour develops immediately. The yarn when dyed is lifted out, wrung, and then it is well washed with water, soaped in a bath at 120° F., with a liquor containing  $\frac{1}{2}$  oz. soap per gallon, then dried. As the cotton yarn is being passed through the developing bath, the latter is freshened up from time to time by suitable additions of the diazo and acetate liquors in the proportions given above. Some dyers use a special form of dye-vat for dyeing paranitroaniline red on yarn, whose construction can be seen from Fig. 35.

The beta-naphthol bath does not keep well and in time tends to grow brown, and when this occurs stains are invariably produced on the cotton. When the yarn or cloth has been prepared with the beta-naphthol, and dried, the developing should be immediately proceeded with, for it is found that by allowing the prepared cotton to lie about it becomes covered with brown stains, and when such stained cotton is passed through the developing bath stains and defective dyeing result. It has been found that by adding a little tartar emetic to the beta-naphthol bath this is largely if not entirely prevented, and the prepared cloth may be kept for a reasonable length of time before proceeding with the development, without fear of stains being formed. Various additions have been made from time to time to the naphthol bath. Some

of these take the form of special preparations of the colour manufacturers, and are sold as naphthol D, naphthol X, red developer C, etc., sometimes gum tragacanth has been added, at others in place of Turkey-red oil there is used a soap made from castor oil with soda and ammonia, but such complicated baths do not yield any better results than the simple preparing liquor given above.

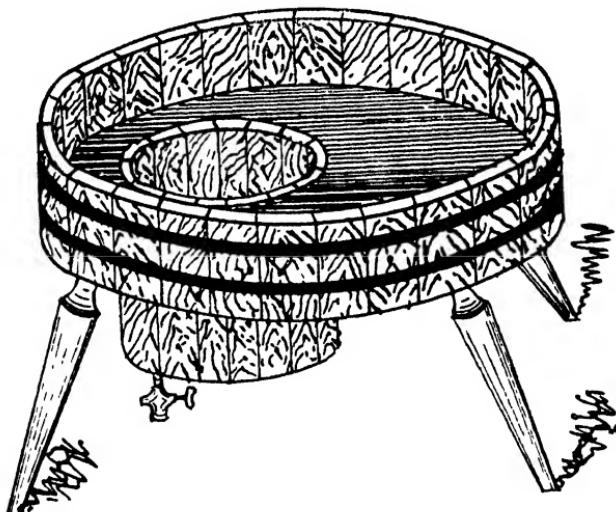


FIG. 35. Dye-tub for paranitroaniline red.

**Dyeing Paranitroaniline Red on Piece Goods.**—The dyeing of this red on piece goods only differs from that on yarns by reason of the difference in the form of material that is dealt with.

1. *Preparing or Grounding.*—The same liquor may be used. This operation is best done on a padding machine, a sketch of which is given in Fig. 34, showing the course of the cloth through the liquor. This is contained in the box of the machine, and this is kept full by a constant stream flowing in from a store vat placed beside the machine. After going through the liquor, the cloth passes between a pair of

squeezing rollers which squeeze out the surplus liquor. Fig. 35 shows a view of a padding machine adapted for grounding paranitroaniline reds. After the padding, the cloth is dried by being sent over a set of drying cylinders, or through what is known as the hot flue.

*2. The Developing.*—After being dried, the pieces are sent through a padding machine charged with the developing liquor made as described above, after which the cloth is rinsed, then soaped, and then washed. Some dyers use a continuous machine for these operations, such as is shown in Fig. 36. While the developing bath used for piece goods may be the same as that used for yarns, some dyers prefer to use one made somewhat differently, thus  $6\frac{1}{4}$  lb. paranitroaniline are mixed with 7 gallons boiling water and  $1\frac{1}{2}$  gallons hydrochloric acid; when dissolved 16 gallons of cold water are added, then, after completely cooling,  $3\frac{1}{2}$  lb. sodium nitrite dissolved in 3 gallons cold water. After twenty minutes, when the diazotisation is complete, water is added to make the whole up to 40 gallons. The acetate liquor is made from  $13\frac{1}{4}$  lb. acetate of soda in  $13\frac{1}{2}$  gallons of water. Equal quantities of these two liquors are used in making the developing bath. Of late years, under the names of Azophor red PN, Nitrazol C, Nitrosamine, etc., there have been offered to dyers preparations of diazotised paranitroaniline in the form of a powder or paste, readily soluble in water, that will keep in a cool and dry place for any reasonable length of time. These are prepared in various ways, and to any dyer who does not want the trouble of diazotising the paranitroaniline they offer some advantages. They produce a red equal in every respect to that obtained from paranitroaniline. The following details show the method to be followed with some of these products, others are very similar to make the developing baths. (1) *Paranitroaniline Red with Nitrazol C.*—Dissolve 25 lb. Nitrazol C in 12 gallons of cold water with

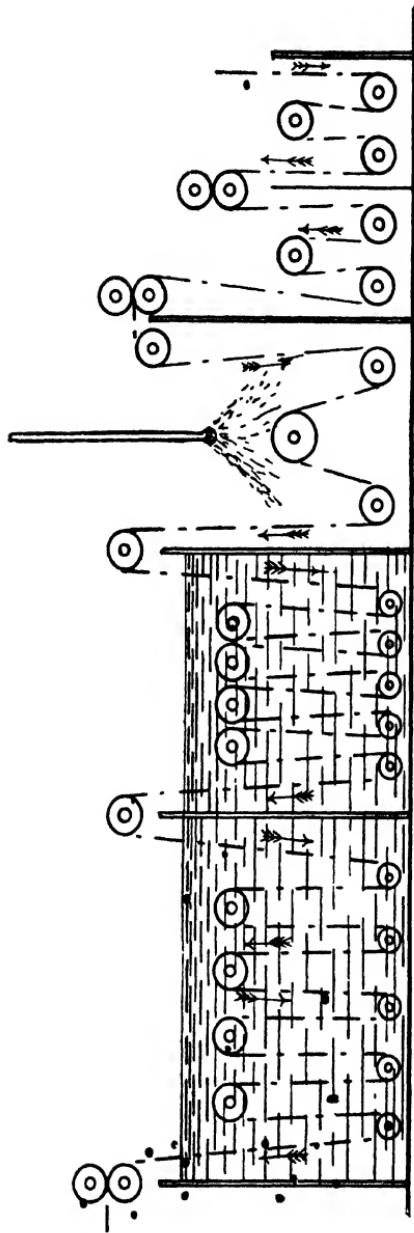


FIG. 36.—Developing machine for para-nitroaniline red.

constant stirring, then add sufficient cold water to make 37 gallons. In another vessel dissolve 11 lb. of acetate of soda in  $5\frac{1}{2}$  gallons water, then add  $1\frac{1}{2}$  gallons caustic soda,  $36^{\circ}$  Tw., mixed with  $5\frac{1}{2}$  gallons water. The developing bath is made by mixing both these solutions. It will suffice for both yarn and piece goods. (2) *Paranitroaniline Red with Azophor Red PN.*—Dissolve  $5\frac{1}{2}$  lb. of Azophor red PN in 4 gallons of water—it dissolves almost completely but usually a few particles of a flocculent character remain undissolved, these can be removed;  $2\frac{1}{4}$  gallons of caustic soda lye of  $36^{\circ}$  Tw. are diluted with water to 10 gallons, and this is added with constant stirring to the Azophor red PN solution. When all is mixed and a clear solution obtained, the developing bath is ready for use, and is used in the same way as the paranitroaniline bath. (3) *Metunitroaniline Orange.*—This orange is produced in the same way as the paranitroaniline red, using metanitroaniline or Azophor orange MN in place of the paranitroaniline or the Azophor red PN given for the red. The quantities of all the materials used are identical. (4) *Nitrosamine Red.*—Dissolve 5 lb. Nitrosamine red in 5 gallons of water and  $2\frac{1}{4}$  lb. hydrochloric acid, when well mixed there is added  $2\frac{1}{2}$  lb. acetate of soda, when all is dissolved add sufficient water to make  $6\frac{1}{2}$  gallons. This bath is used exactly in the same way as the paranitroaniline developing bath, and it produces identical results in every way. (5) *Paranitroaniline Brown.*—By boiling the paranitroaniline red dyed cotton in a weak bath of copper sulphate a very fine fast brown, resembling a cutch brown, is produced. A better plan, however, is to prepare the cotton with a ground containing an alkaline solution of copper, 3 lb. beta-naphthol are dissolved in 5 pints of caustic soda lye of  $36^{\circ}$  Tw., to which is added 5 lb. Turkey-red oil and 10 pints alkaline copper solution, water being added to make 13 gallons of liquor. The cotton is treated in this way as with the ordinary beta-

naphthol preparation. The alkaline copper solution is made by taking 5 pints of copper chloride solution at  $76^{\circ}$  Tw., sp. gr. 1.08, adding  $3\frac{1}{4}$  lb. tartaric acid, 6 pints caustic soda lye,  $70^{\circ}$  Tw., and 2 pints of glycerine. The developing bath for the brown is the same as for the paranitroaniline red, or the Azophor red PN bath may be used. (6) *Toluidine Orange*.—For this colour the cotton is prepared with the beta-naphthol in the ordinary way. The developing bath is made from 2 lb. orthonitrotoluidine mixed with 12 pints boiling water and  $2\frac{1}{2}$  pints hydrochloric acid ; when dissolved allow to cool and then add  $12\frac{1}{2}$  lb. ice. When thoroughly cold stir in  $2\frac{1}{2}$  pints of sodium nitrite solution containing 3 lb. per gallon. Stir well for twenty minutes, then filter ; add 4 lb. sodium acetate and sufficient ice-cold water to make 13 gallons. Use this bath in the same way as the paranitroaniline bath. (7) *Beta-naphthylamine Red*.—This red is a good one, but is not so bright or so fast as the paranitroaniline red, hence although somewhat older in point of time it is not dyed to the same extent. The developing bath is made from  $1\frac{1}{2}$  lb. beta-naphthylamine dissolved with the aid of 10 pints boiling water and 1 pint hydrochloric acid. When dissolved allow to cool ; add 27 lb. ice and 2 pints hydrochloric acid. When cooled to  $32^{\circ}$  to  $36^{\circ}$  Tw., add 3 pints sodium nitrite solution (3 lb. per gallon) and 4 lb. sodium acetate, making up to 13 gallons with water. This also is used in precisely the same way as the paranitroaniline red developing liquor. (8) *Alpha-Naphthylamine Claret*.—This is a very fine and fairly fast red, and next to the paranitroaniline red may be considered the most important of the naphthol colours. The developing bath is a little more difficult to make, owing to the fact that it is more difficult to get the alpha-naphthylamine into solution. The best way of proceeding is the following : Heat  $1\frac{1}{2}$  lb. of alpha-naphthylamine in 10 pints of boiling water, agitating well until the base is very finely

divided in the water, then  $1\frac{1}{4}$  pints of hydrochloric acid is added, and the heat and stirring continued until the base is dissolved, then the mass is allowed to cool, 27 lb. of ice is added, and  $1\frac{1}{2}$  pints of hydrochloric acid. When cooled down to  $32^{\circ}$  to  $36^{\circ}$  F., there is added 3 pints sodium nitrite solution (3 lb. per gallon), and after allowing the diazotisation to be completed, 4 lb. sodium acetate and sufficient water to make 13 gallons of liquor. The bath is used in the same manner as the previous developing baths. (9) *Dianisidine Blue*.—Dianisidine develops, with beta-naphthol, a violet blue, which is not very fast, but by the addition of some copper to the developing bath a very fine blue is got which has a fair degree of fastness. The developing bath is made as follows : Mix  $10\frac{1}{2}$  oz. dianisidine with 7 oz. hydrochloric acid and  $7\frac{1}{2}$  pints of boiling water, when complete solution is obtained it is allowed to cool, then 20 lb. of ice is added ; next  $1\frac{3}{4}$  pints of nitrite of soda solution containing  $1\frac{1}{2}$  lb. per gallon and  $2\frac{1}{2}$  pints of cold water. Stir for thirty minutes, then add  $1\frac{1}{4}$  pints copper chloride solution at  $72^{\circ}$  Tw.. and sufficient water to make up  $6\frac{1}{2}$  gallons. The cotton is prepared with beta-naphthol in the usual way, and then passed through this developing bath. (10) *Amidoazotoluol Garnet*.—Amidoazotoluol produces with beta-naphthol a fine garnet red in the usual way.

The developing bath is made from 14 oz. amidoazotoluol, mixed with  $1\frac{1}{2}$  pints of sodium nitrite solution containing  $1\frac{1}{2}$  lb. per gallon ; when well mixed add 1 pint of hydrochloric acid diluted with 2 pints water ; when this is well mixed add sufficient water to make up a gallon, then add 1 lb. acetate of soda.

The cotton is passed through this dye-bath, then washed well, passed through a weak acid bath, then soaped well, washed and dried.

More recently the Griesheim Elektron Co. have intro-

duced Naphthol AS as a substitute for beta-naphthol. This product has the great advantage that there is no necessity to dry the "prepared" cloth before immersing it in the diazo solution. Even more recently, other substitutes—Naphthol AS.BS, Naphthol AS.BO and Naphthol AS.RL have been introduced to dyers, and these compounds are various substituted anilides of beta-hydroxynaphthoic acid. Further development of these compounds is now proceeding.

#### 8. DYEING WITH REDUCED DYESTUFFS FOLLOWED BY OXIDATION.

As previously indicated, this method of dyeing is adopted in connection with vat and sulphur dyestuffs.

*Sulphur Dyes.*—In the usual method for applying these dyes the colour is first dissolved in a hot solution containing sodium sulphide and sodium carbonate. Equal parts of dye and sodium sulphide are used, although in the case of sulphur blues somewhat more sulphide should be used. Probably the sulphur blacks are the most largely used of sulphur dyes and these are easily soluble when an equal weight of sodium sulphide is used. They are used for hosiery, but also to a greater extent for cotton piece goods, the dyeing being carried out in a jig. The sodium carbonate is used to assist the solubility of the dyestuff and also to prevent decomposition of the dye solution when in contact with acidic substances. For instance, addition of hydrochloric acid to a solution of a sulphur dye dissolved in sodium sulphide alone, would result in liberation of sulphuretted hydrogen and precipitation of the sulphur dye. When sodium carbonate is also present, this must be neutralised before liberation of sulphuretted hydrogen can occur.

All sulphur dyes contain free sulphur, and this to some extent is always deposited on the dyed fabric. Although

this would be supposed to be quite harmless, it is found in the case of fabric dyed with sulphur black, that this sulphur tends to oxidise to form sulphuric acid. Consequently the sulphur-dyed fabrics are liable to become tender during storage. Experiment has shown that metallic catalysts such as copper and iron assist the free sulphur to oxidise to sulphuric acid. Hence it is not advisable to after-treat sulphur black dyed fabrics with a bichromate or copper sulphate. Moreover, in order to avoid all risks of tendering, all fabrics dyed with sulphur dyestuffs should finally be left, having a slightly alkaline reaction.

Generally, sulphur dyes do not exhaust well, so that a considerable amount of dyestuff always remains in the dye liquor. Hence, wherever possible, the dye-baths should be used repeatedly, the loss of dye being replenished after each dyeing. Furthermore, the addition of salt during dyeing is necessary since this very considerably increases the rate at which the cotton fabric absorbs the sulphur dye.

In the actual process of dyeing the fabric is given several ends through the boiling dye liquor contained in a jig, salt being occasionally added to increase the exhaustion of the dye liquor, and it is then well washed with water. During the washing, the fabric is unavoidably exposed to the air and so that the dyed fabric becomes oxidised to its proper colour. The oxidation is completed during the processes of mangleing and drying.

Sulphur blacks oxidise very readily, but in the case of sulphur blues it is advisable to assist the aerial oxidation by passing the dyed fabric through water containing hydrogen peroxide. This treatment also brightens the shade considerably.

In general, however, after oxidation of the dyed fabric is most conveniently carried out by means of sodium bichromate and acetic acid. The dyed fabric should then be given

3 to 4 ends in a liquor containing 2 per cent. of sodium bichromate and 2 per cent. of acetic acid at 75° C. After washing in water, the fabric may then be mangled and dried, the sulphur colour being then in its highest state of oxidation.

One fault characteristic of dyeing with sulphur colours is that the dyed fabrics frequently have edges deeper in shade than the remainder of the fabric. Or, the whole fabric appears to have a bronzy sheen. This fault is due to the ease with which the sulphur dyes are oxidised by the air, but it is generally overcome by using an increased quantity of sodium sulphide in the dye-bath. To correct such a faultily dyed fabric, it should be passed several times through a hot solution of sodium sulphite, whereby the bronziness is removed and the shade levelled : it may then be redyed.

*Vat Dyestuffs.*—These dyestuffs, which generally yield very fast dyeings, although there are several definite exceptions, may be divided into three classes :—

Indigoid dyes.

Anthraquinone dyes.

Sulphur vat dyes.

The indigoid dyestuffs were discovered subsequent to the elucidation of the chemical structure and synthesis of natural indigo, and they include Thioindigo red, Ciba scarlet, Ciba violet, Helidone orange R, Helidone fast scarlet R and Ciba red C.

Indigo itself has been used in dyeing for about 2000 years, and, its application being of considerable importance, will therefore be considered separately.

Indigo practically always reaches the dyer as an insoluble paste, and to enable it to be dissolved and therefore to be used as a dye, the indigo has to be reduced. The colouring principle of indigo is a body named indigotin, to which the formula  $C_{16}H_{16}N_2O_2$  has been given. When indigo is mixed

with substances like lime and copperas, lime and zinc, zinc and bisulphite of soda, which cause the evolution of nascent hydrogen, it takes up this body and passes into another substance which is called indigo white that has the formula  $C_{16}H_{12}N_2O_2$ , leuco, or white indigo ; this substance is soluble in water, and so when it is formed the indigo passes into solution and can then be used for dyeing. But indigo white is an unstable substance on exposure to air : the oxygen of the latter attacks the hydrogen which it has taken up, and indigotin is reformed, the indigo white changing again into indigo blue.

Indigo dyeing consists of three operations :—

(1) Preparation of the indigo solution, or, as it is called, setting the dye-vat. (2) Steeping the cotton in this vat. (3) Exposing to the air. There are several methods of preparing, or setting the dye-vat, and of each of these modifications are in use in every indigo dye-house : —

(1) With lime and copperas. (2) Zinc and lime vat. (3) Zinc and bisulphite of soda.

The dye-vats may be either round tubs or square wooden tanks ; when cloths or wraps are being dyed these may be fitted with winches and guide rollers, so as to draw the materials through the liquor. In the case of yarns in hanks these appliances are not necessary. Fig. 37 is a sketch of an indigo dye-vat for cloth or warps.

1. **Lime and Copperas Vat and how to Use it.**—To prepare this vat take 75 gallons of water, 4 lb. of indigo, 8 lb. copperas, and 10 lb. of good quicklime. Put these into the vat in the order shown. The amount of indigo is added in proportion to the shade which is required to be dyed : for pale shades, 2 lb. to 3 lb. will be sufficient ; while for deep shades, 6 lb. to 7 lb. may be used. The amount of copperas should be from one and a half to twice that of the indigo. The vat should be stirred very well and then left to stand. The

changes which occur are probably the following. The lime acts upon the copperas and produces ferrous hydrate--this is unstable and tends to take up oxygen and hydrogen from the water, particularly when there is some indigo present, and forms ferric hydrate ; hydrogen is at the same time liberated, and combines with the indigo to form the soluble indigo white. It takes about twenty-four hours to make an indigo

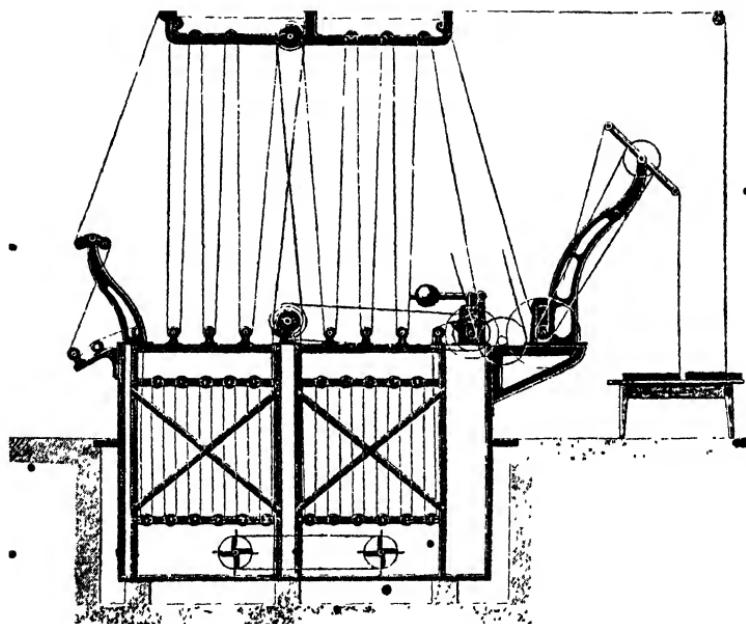


FIG. 37.—Indigo dye-vat for cloth.

vat. When properly made and in good condition, the liquor will be clear and of a brownish-yellow colour, a bluish scum may collect on the surface. If the liquor appears at all greenish it is an indication that the indigo has not been completely reduced, and the vat needs a further addition of lime and copperas, which should be of good quality. Too much of each should not be used, because with them there is

formed at the bottom of the vat a sediment of calcium sulphate and ferric hydrate, and it is not wise to increase this to too great an extent, which would be the case if too much lime and copperas were added. Any scum on the surface is raked on one side, the cotton yarn immersed for a few minutes, then it is taken out, wrung, allowing the excess liquor to flow back into the vat, and the yarn hung up in the air for the blue to develop. The depth of shade which is dyed depends chiefly upon the amount of indigo in the vat, and also upon the time during which the hanks are dipped in the liquor. Light and medium shades can be readily and conveniently got by a single dip, but deep shades are best got by repeating the dipping once or twice as occasion demands. Deep shades got by using a strong bath at a single dip are found to rub badly, while by repeated dips the dye gets more into the substance of the fibre, and therefore the colour is more firmly fixed and it rubs less. Some indigo dyers have quite a range of vats, using those fresh made for dyeing deep shades, while the old vats being nearly exhausted are used only for light shades, and finally, when completely exhausted, are thrown away. After the day's work the vat should be stirred up and then allowed to stand. If necessary it may be strengthened by the addition of fresh quantities of indigo, lime and copperas : the next morning it will be ready for use. Generally a lime-copperas vat will remain in good working order for about a month, when it will be necessary to throw it away.

**2. Zinc and Lime Vat.**—Zinc dust is a bye-product in the process of zinc extraction. It is a grey, very heavy powder, consisting mostly of finely divided metallic zinc, with traces of oxide and sulphide of zinc. Of these only the metallic zinc is active in reducing the indigo, the rest of the ingredients are not of any consequence. The valuation of zinc dust is a very difficult operation, but it is desirable that this be

done, as the product is liable to be very variable in the proportion of actual zinc it contains, and it will pay large buyers always to have it tested. Zinc dust must always be kept in a dry place. For the reduction of zinc powder lime is chiefly used. The following are two good mixtures. Vat with zinc and lime : 10 lb. indigo, dry and ground fine ;  $5\frac{1}{2}$  lb. zinc dust ; 22 lb. slaked lime, dry.

The vat is set as follows : A part of the lime is mixed with the indigo, and the two bodies are well mixed together and allowed to stand for ten minutes, then the zinc powder is added. It is best to make this into a smooth paste with water before adding it to the other ingredients, then the rest of the lime is added and the whole is thoroughly stirred together with the necessary quantity of water.

Vat with zinc powder, lime and soda : 10 lb. indigo, dry and ground fine ; 10 lb. zinc powder ; 10 lb. slaked lime, dry ; 35 lb. caustic soda at  $11^{\circ}$  Tw., sp. gr. 1.055. Add the lime to the ground indigo, then add the zinc and finally the soda lye. Soon after the various ingredients of the vats are added together the whole mass becomes hot, when it must be well stirred. It soon begins to evolve gas and the mixture froths. In from two to four hours the evolution of gas ceases. The dark blue solution now becomes yellow and the liquor shows all the characteristics of the indigo vat. It is necessary to keep the vat well stirred up during the time of setting, which takes from five to six hours. If there is much evolution of gas after this time it indicates that too much zinc powder has been added ; this is a common fault with dyers, and such excess causes the vat to be too much disturbed and to work dirty. A lime-zinc vat, with occasional additions of new materials, keeps good for three months, and even then is in a better condition than the copperas vat. This vat is used in precisely the same way as the copperas vat ; as it contains no sediment, or but little, it works cleaner than the copperas vat, and as a

rule the indigo blues dyed in it are faster to rubbing. After a day's work it can be well stirred up and fresh additions of lime, zinc and indigo made to bring it up to its original dyeing strength.

**3. Zinc-Bisulphite Indigo Vat.**—When zinc dust and bisulphite of soda are mixed together a reaction sets in, the zinc dissolves, and there is formed sodium hydrosulphite and zinc and sodium sulphites. If now indigo is mixed with this solution the sodium hydrosulphite exerts a reducing action on it, forming white indigo and sodium sulphite, a perfectly clear solution being obtained, which may be used in dyeing cotton or wool. With this vat it is customary to prepare a strong stock solution of reduced indigo, and to add this to the dyeing-vats as may be required.

*To Make the Stock Liquor.*--Take 20 lb. of indigo, grind into a paste with 20 gallons of boiled water, then add 25 lb. lime slaked into a milk. In a separate tub there is mixed 80 lb. bisulphite of soda, 70° Tw., sp. gr. 1·350, with 9 lb. zinc dust ; this mixture is well stirred and every care taken to prevent it getting hot. When the zinc has dissolved and the mixture is free from any sulphurous smell it is run into the indigo mixture given above. The whole is well stirred together for some time, and then at intervals, until the indigo has become dissolved, sufficient water is added to make up 50 gallons, when the stock liquor will be ready. It should have a deep yellow colour. The surface may have a scum of a bronzy colour collect on it. This stock liquor should be kept in casks free from exposure to the air. To make the working vat from this stock liquor the following is the method of proceeding : Water is run into the vat, and this is heated from 70° to 80° C. in order to expel air from it, after which it may be allowed to cool, then for each 1000 gallons contained in the vat there is added 30 lb. bisulphite of soda, 3 lb. zinc dust and 3 lb. lime, made into a cream. When all these in-

gredients are dissolved a quantity of the stock liquor is added in proportion to the shade that it is desired to dye. The whole is well stirred, then the vat is allowed to rest for half an hour to enable any sediment to settle, and then the dyeing is proceeded with. Should the vat show signs of becoming green in colour it is a good plan to add a mixture of 1 lb. zinc dust and 10 lb. bisulphite of soda. The vat should be kept alkaline, and so a little lime may be added from time to time. After a day's work it is well to add a little of the zinc and bisulphite mixture, to stir well and allow to stand overnight ; the next morning strengthen up the vat by adding fresh stock liquor. In place of using lime in making up the vat it is possible to use a mixture of caustic soda and ammonia. The lime will tend to cause some sediment to form in the vat, whereas the soda and ammonia will not. When they are used the following mode of working may be followed :—

*Stock Liquor.*—Soda zinc vat : Put in a tub 26 gallons cold water, 15 lb. zinc powder ground into a paste with 6 gallons water, then stir in 8 gallons bisulphite of soda at 60° Tw., stir well, keeping the heat down as much as possible, after which add 8 pints caustic soda lye at 70° Tw. and 14 pints 20 per cent. liquor ammonia. When all is thoroughly mixed add 30 lb. indigo, ground into a paste with 7 gallons water, allow to stand for half an hour, then add water to make 100 gallons, stir at intervals for twelve hours or so, when the stock liquor will be ready for use. This is used to make the vat in the same way as the first above described. It is necessary before adding the stock liquor in making a vat to destroy any oxygen or air which is present in the vat. This may most conveniently be done by adding thereto a solution of hydrosulphite of soda, which may be made by mixing 4½ lb. zinc dust with 5 gallons of water and 3 gallons bisulphite of soda at 70° Tw., sp. gr. 1·350, stirring well, so that the temperature does not rise too high, there is then

added 2 pints caustic soda and 3 pints liquor ammonia, 20 per cent. ; when all is dissolved, water is added to make up 13 gallons. Should the vat show signs of becoming charged with indigo, indicated by its becoming of a green colour, a little of this hydrosulphite added from time to time will correct it. The hydrosulphite-indigo vat made by either of the two methods indicated above works well, and with due care may be kept in work for months. It gives good shades of indigo, although some dyers consider that these have not the rich bronze hue got from the lime and copperas vat. The shades are rather faster to rubbing. It has been proposed to employ the dyestuff indophenol in conjunction with indigo, in which case the method of making the vat is with zinc, bisulphite of soda, caustic soda, and ammonia as last described, only in place of using all indigo a mixture of 22 lb. indigo and  $7\frac{1}{2}$  lb. indophenol is used. Good blue shades of considerable fastness can thus be obtained.

In place of zinc and bisulphite, sodium hydrosulphite itself may be used as a reducing agent in the indigo vat, and of course, this substance is more convenient to handle. In this method, the stock vat is set with 30 gallons of water, 9 gallons of caustic soda of 76° Tw., and 150 lb. of 20 per cent. indigo paste. After warming to 40° to 50° C., sodium hydrosulphite (about 25 lb.) should be added until the indigo is completely reduced. The liquor is then ready for addition to the main vat, and has the important advantage that it contains no obnoxious sediment.

A characteristic of the anthraquinone *vat* dyestuffs is that they require to be dyed from a dye liquor containing about  $\frac{1}{2}$  per cent. of caustic soda, in order that they may be completely soluble. For this reason, these dyestuffs are not applied to woollen fabrics, since they would suffer serious deterioration.

The dye liquor is usually prepared by heating a suitable

solution of caustic soda to about  $40^{\circ}$  C., then adding the necessary amount of sodium hydrosulphite in the solid form, and subsequently adding the vat dyestuff (such dyes are almost always sold in the form of a paste). Reduction of the dyestuff to its soluble form by the action of hydrosulphite is complete within a few minutes. The bleached cotton material may then be entered in the dye liquor, both cotton and liquor being guarded as much as possible from aerial oxidation. The temperature should then be gradually raised to about  $55^{\circ}$  to  $60^{\circ}$  C. and after about one hour at this temperature, dyeing is usually complete. The fabric should then be rinsed in warm water containing about 1 per cent. of sodium hydrosulphite, then in warm water and afterwards soaped at the boil in a solution containing 1 lb. of soap and  $\frac{1}{2}$  lb. of sodium carbonate per 30 gallons.

Some vat dyes (e.g. Caledon Red BN) are dyed at temperatures not exceeding  $30^{\circ}$  C.

The soaping not only frees the cotton from loosely adhering colour, but it also brightens the shade and renders it faster to washing and light, etc. Soaping is therefore a definite part of the dyeing process.

For most vat colours the composition of the dyeing liquor is that stated in the following table:—

COMPOSITION OF DYE-BATH FOR 100 LB. COTTON.

Water . . . .	200 galls. = 20-25 times weight of yarn.										
Caustic soda . . .	4 galls. $53^{\circ}$ Tw.										
Dyestuff in paste, ordinary strength (in lb.)	½	1	2	3	5	10	15	20	30	40	50
Hydrosulphite concentrated powder (in lb.)	2	2	2	2	2	2½	3½	4½	6½	8	8

The properties of several vat dyestuffs are also indicated in the following table :—

	Vatting.	Chlorine.	Ketone.	Macerating.	Stoving.	Aerial (Cross) Dyeing.	Chrome Cross Dyeing.	Colour of Dye-bath.
Duranthrene yellow G extra paste	4	5	5	1.2	5	5	5	Royal blue.
golden-orange Y paste	3.4	5	5	3.4	5	5	5	Magenta.
“ red 5 (G)Y paste	5	4	5	2.3	5	5	5	Claret.
“ BN paste	5	4.5	5	2.3	5	5	5	Red.
“ Bordeaux P paste	3.4	4.5	5	4	5	5	5	Orange-brown.
“ red-violet 2 RN paste	5	4.5	5	2.3	5	5	5	Violet.
Brown B paste	4	4	Not fast.	—	5	5	4	Grey.
olive GJ powder	4	4.5	—	—	5	5	4	Blue.
blue 3 GT paste	5	5	2.3	—	5	5	3.4	Not fast. Blue.
“ GCD paste	5	5	3	5	5	5	5	—
“ CC paste	5	5	3.4	3	5	5	4	—
“ RD extra paste	5	5	*	3	5	5	5	Not fast.
“ dark blue BO paste	4	4	5	3.4	5	5	5	Violet.
“ brilliant violet R powder	5	4.5	5	3	5	5	5	Red.
Durindone red Y “	—	3.4	5	—	5	5	5	—
“ B “	2	2	5	—	3.4	5	4.5	—
“ 3 B “	3.4	4	5	—	5	5	5	—
“ blue 4 B “	2	4	3	—	5	5	5	—
“ 5 B “	2	4	3	—	4.5	5	5	—
“ 6 B “	2	4	3	—	4.5	5	5	—

\* Duranthrene blue RD extra turns much greener with chlorine, but the original shade can be restored by a treatment with hydrosulphite. Dianthrone blues CC and GCD are affected by chlorine to a much less extent : with these also, any change can be corrected by hydrosulphite.

Note.—In the following tables of fastness, No. 5 represents the highest and No. 1 represents the lowest degree of fastness.

In some instances (e.g. Caledon jade green, Caledon yellow G, and Caledon blue GCD), the shade of the dyed fabric does not develop quickly by aerial oxidation. Hence,

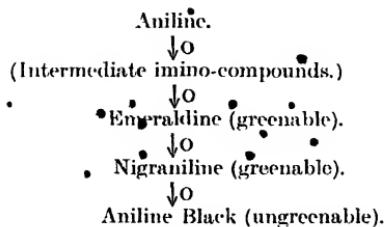
the dyed fabric after rinsing should be treated at 50° G. in a liquor containing  $\frac{1}{2}$  per cent. of sodium perborate.

The indigoid and sulphur vat dyestuffs are usually more soluble when reduced than the vat dyes of the anthraquinone series. Hence, although dyed by very similar methods, they require for solution about 25 per cent. less caustic soda and slightly less hydrosulphite.

*Aniline Black.*—This is not by any means an easy colour to dye, but still with careful attention to carrying out the various operations in detail excellent results can be obtained. Aniline black is the fastest black which is known ; it resists, when well dyed, exposure to air and light ; is quite fast to washing and soaping. Its disadvantages are that there is, with some methods of working, a tendency to tender the cotton fibre, making it tear easily : secondly, on exposure to air it tends to turn green, this however only happens when the black has not been dyed properly.

Aniline black is produced direct upon the cotton fibre by various processes which involve the oxidation of aniline, and though this black has been known for at least fifty years it has not been yet superseded. In fact, it is stated that one-half of the world's production of aniline is used in dyeing fabrics with aniline black.

The chemical composition and constitution of aniline black has been thoroughly investigated and many theories have been put forward to explain its formation. At present, aniline black is considered to be formed in the following stages :—



Aniline black is usually dyed by either of two processes. In the *single-bath* method, cotton material is immersed in a liquor containing aniline, an acid, a catalyst, and an oxidant, the mixture being heated. As the oxidation proceeds, aniline black is formed partly in the bath and partly within the cotton fibres. The method is therefore somewhat uneconomical but is used for dyeing loose cotton for which the *ageing method* is not suitable.

Before dyeing aniline black by the single-bath process, the cotton should be well scoured with sodium carbonate and thoroughly washed; bleaching is of course unnecessary. It should then be entered into a bath containing the following :—

Aniline salt . . . . .	13 lb.
Hydrochloric acid 32° Tw. . . . .	22 ,,
Sodium bichromate . . . . .	14 ,,
Water . . . . .	200 gallons.

The temperature of the bath should be gradually raised to 70° C. and when the full black shade is developed, the cotton material should be taken out, thoroughly washed and soaped in a  $\frac{1}{2}$  per cent. hot soap solution and afterwards dried.

Alternatively a dye-bath having the following composition :—

Aniline salt . . . . .	14 lb.
Sodium bichromate . . . . .	13 ,,
Copper sulphate . . . . .	2 ,,
Hydrochloric acid, 32° Tw. . . . .	23 ,,
Water . . . . .	200 gallons.

may be used. In this bath the cotton is worked for about 1 hour, during which time the temperature is gradually raised

- to the boil. Afterwards, the material is worked in a bath containing :—

Copperas . . . . .	4 lb.
Sulphuric acid . . . . .	6 ,,
Water . . . . .	200 gallons.

for about ten minutes at 95° C., and is then washed, soaped and dried.

Piece goods, however, are never dyed by the single-bath method, since the resulting dyeings are liable to rub and they have not the maximum fastness. Fabrics are therefore dyed by a method in which the fabric continuously passes through a padding liquor containing the necessary chemicals for the production of the black, and is then dried and passed through a warm moist atmosphere whereby the black is developed. Subsequently, the developed fabric is then passed through a solution of a bichromate so that the black may be completely oxidised to an ungreenable shade, and then, after being thoroughly washed, the fabric is dried.

The composition of the padding liquor varies considerably, but two types are largely used and they are distinguished from each other chiefly because one contains copper sulphate and the other sodium ferrocyanide as a catalyst. Vanadium salts and copper sulphide are alternative catalysts, but as they are not much used except in textile printing they will not be described here.

A typical copper-black padding liquor contains :—

Aniline hydrochloride . . . . .	120 lb.
Copper sulphate . . . . .	5½ ,,
Sodium chlorate . . . . .	38 ,,
Ammonium chloride . . . . .	4 ,,
Aluminium acetate, 15° Tw. . . . .	4½ ,,
Water Sufficient to make a total vol. of 100 gallons.	

The ammonium chloride is added so that during the development of the black, the fabric will not become bone-dry—a state in which considerable tendering of the fabric may take place. Further, the aluminium acetate is added with this same object, since being a basic salt it serves to neutralise part of the harmful mineral acid which is liberated during the development of the black.

When this copper-black padding liquor is employed, the impregnated fabric is not usually dried on the usual drying cylinders, since the risk of tendering is too great. It is, therefore, dried and developed while passing through a large chamber generally known as a Mather Platt ager (see Fig. 44). In this chamber, the fabric passes over a large number of wooden winces, and the temperature is maintained at 50° to 60° C., steam being cautiously injected so as to maintain a moist atmosphere. When leaving the ageing chamber, the fabric is of a dark bottle green colour, this being oxidised to a full black by after-chroming it with a  $\frac{1}{2}$  per cent. solution of sodium bichromate at about 60° C. The copper black process requires careful attention, since the cotton easily becomes tendered if the ageing is carried out at too high a temperature, or if the fabric is allowed to become too dry.

On the other hand, the *prussiate-black* method is safer, since excess of aniline oil may be used in the padding liquor of which the following composition is typical :—

Aniline salt . . . . .	75 lb.
Aniline . . . . .	10 "
Sodium chlorate . . . . .	35 "
Sodium ferrocyanide . . . . .	52 "
Water . . . . .	80 gallons.

After being padded in this liquor, the fabric is almost dried on the usual drying cylinders; and is then passed through a Mather Platt ager (somewhat smaller than that

used in copper black dyeing) the temperature being maintained at 95° to 100° C. and moisture being present. The fabric, leaving this apparatus, is black in colour and is rendered ungreenable by after-chroming in much the same manner as for the copper black.

Fabrics dyed with a prussiate black are usually stronger than those dyed with a copper black.

A sample of well-dyed aniline black fabric should not show appreciable signs of greening when boiled for two minutes in a 5 per cent. solution of sodium bisulphite.

During recent years two improved processes for dyeing cotton fabrics with aniline black have been developed. In one of these, aniline is wholly or partly replaced by *p*-amino-diphenylamine or a related substance such as *p*-amino-*p*'-hydroxydiphenylamine.

These diphenylamine compounds are more easily oxidised than aniline and, furthermore, the resulting black is ungreenable, it being unnecessary to employ an after-chroming treatment.

Unfortunately, *p*-amino-diphenylamine hydrochloride is not easily soluble in cold water, so that the base is usually employed in the form of its more soluble salts formed with organic acids such as lactic, acetic and formic acids.

A padding liquor suitable for use with this process is prepared by mixing equal volumes of the following solutions A and B :—

*Solution A.*

Gum tragacanth . . . . .	6½ lb.
<i>p</i> -amino-diphenylamine . . . . .	40 ,,
Lactic acid, 50 per cent. . . . .	50 ,,
Acetic acid . . . . .	130 ,,
Total volume . . . . .	50 gallons.

*Solution B.*

Aluminium chloride, 53° Tw.	. . . . .	25 lb.
Chromium chloride, 53° Tw.	. . . . .	25 ,,
Cupric chloride, 77° Tw.	. . . . .	4 ,,
Sodium chlorate	. . . . .	30 ,,
Turpentine	. . . . .	10 ,,
Total volume	. . . . .	50 gallons.

In dyeing, the fabric is padded in the usual manner, dried and steamed in the Mather Platt ager for two to three minutes. It is then washed without chroming, soaped hot and dried. The absence of mineral acids in the padding liquor enables tendering to be largely avoided. *p*-amino-diphenylamine, however, is much dearer than aniline and is not available at the present time. It therefore seems likely that this process is not being worked to any large extent.

Instead of using *p*-amino-diphenylamine alone, it may be used in admixture with as much as 75 per cent. of aniline, but the resulting shades are not then so fast to greening.

In the second improved process, advantage is taken of the fact that the oxidation of aniline is much accelerated by the presence of certain amines or aminophenols, such as *p*-phenylene diamine, *p*-amino-phenol.

Green, who discovered this, subsequently devised a process for dyeing aniline black in which *p*-phenylene diamine is used as a catalyst. This substance so facilitates the formation of the black that the presence of free mineral acid in the aniline black padding liquor is unnecessary, and indeed an oxidant such as sodium chlorate may be dispensed with. In practice, however, aerial oxidation is not satisfactory, so that a chemical oxidant is used.

A typical padding liquor for use in Green's process has the following composition :—

Aniline . . . . .	50 lb.
Paraphenylene diamine . . . . .	4 ,,
Formic acid, 90 per cent. . . . .	30 ,,
Ammonium chloride . . . . .	140 ,,
Sodium metabisulphite . . . . .	14 ,,
Cupric chloride . . . . .	48 ,,
Total volume . . . . .	250 gallons.

In preparing the above liquor, the cupric chloride, ammonium chloride and sodium metabisulphite are dissolved together, whereby a solution containing cuprous chloride is produced. This solution is then added to the remainder of the padding liquor. A padding liquor containing cuprous chloride is more stable than one containing the copper catalyst in the cupric state.

- After being padded in the usual manner with the above liquor, the fabric is dried, aged and after-chromed in the usual manner.

By means of Green's process, a good aniline black may be obtained and the process has the advantage that it is less dangerous to the employees who work it.

## CHAPTER V.

### DYEING UNION (MIXED COTTON AND WOOL) FABRICS.

THERE is now produced a great variety of textile fabrics of every conceivable texture by combining the two fibres, cotton and wool, in a number of ways ; the variety of these fabrics has of late years considerably increased, which increase may be largely ascribed to the introduction of the direct dyeing colouring matters—the Diamine dyes, the Benzo dyes, the Congo and the Zambesi dyes, for in the dyeing of wool-cotton fabrics they have made a revolution. The dyer of union fabrics, that is, fabrics composed of wool and cotton, formerly found great difficulty in obtaining uniform shades on the fabrics supplied to him, owing to the difference in the affinity of the two fibres for the dyestuffs then known. Now the direct dyes afford him a means of easily dyeing a piece of cotton-wool cloth in any colour of a uniform shade, while the production of two-coloured effects is much more under his control, and has led to the increased production of figured-dress fabrics, with the ground in one fibre (wool) and colour, and the design in another fibre (cotton) and colour. The number of direct dyes made by the various colour manufacturers is now very great. To obtain good results it is necessary that the dyer of union fabrics should have a thorough knowledge of the dyes he is using, for each dye makes a rule to itself as regards its power of dyeing wool and cotton—some go better on to the cotton than on to the wool, and *vice versa*. Some dye wool best at the boil, others

equally well below that heat; some go on to the cotton at a moderate temperature, others require the dye-bath to be boiling; some will go on to the cotton only, and appear to ignore the wool. The presence or absence in the dye-bath of such bodies as carbonate of soda, Glauber's salt, etc., has a material influence on the degree of the affinity of the dyestuff for the two fibres, as will perhaps be noted hereafter. Again, while some of the dyes produce equal colours on both fibres, there are others where the tone is different. With all these peculiarities of the Diamine and other direct dyes the union dyer must make himself familiar. These dyes are used in neutral baths, that is, along with the dyestuff. It is often convenient to use, along with the direct dyes, some azo or acid dyes, which have the property of dyeing the wool from neutral baths; many examples of such will be found in the practical recipes given below. The dyes now under consideration may be conveniently classed into five groups.  
(1) *Those dyes which dye the cotton and wool from the same bath to the same shade, or nearly so.*—Among such are Thioflavine S, Diamine fast yellow B, Diamine orange B, Diamine rose BD, Diamine reds 4B, 5B, 6B and 10B, Diamine fast red F, Diamine Bordeaux B, Diamine brown N, Diamine browns 3G, B and G, Diamine blues RW, BX, Diamine blue G, Diamine greens G and B, Diamine black HW, Diamine dark blue B, Union blacks B and S, Oxydiamine blacks B, M, D and A, Diamine catechine G, Union blue BB, Oxyphenine, Chloramine yellow, Alkali yellow R, Chromine G, Titan scarlet S, Mimosa, Curcumine, Primuline, Auroline, Congo Corinth B, Thiazole yellow, Columbia yellow, Oxydiamine yellow GG, Oxydiamine oranges G and R, Diamine orange F, Oxydiamine red S. (2) *Dyes which dye the cotton a deeper shade than the wool.*—The following belong to this group: Diamine fast yellow A, Diamine oranges G and D, Diamine catechine G, Diamine catechine

B, 'Diamjne sky blue, Diamine' blue 2B, Diamine blue 3B, Diamine bl̄ue BG, Diamine brilliant blue G, Diamine new blue R, Diamine steel blue L, Diamjne black RO, Diamine black BO, Diamine black BH, and Oxydiamine black SOOO, Diamine nitrazol brown G, Diamine sky blue FF, Diamine dark blue B, Diamine Bordeaux B, Diamine violet N, Oxydiamine violet B, Columbia blacks B and FB, Zambesi black B, Congo brown G, Direct yellow G, Direct orange R, Clayton yellow, Cotton yellow, orange TA, Benzo purpurine B, Brilliant Congo R, Chicago blues B an 4Bd and 6B.

(3) *Dyes which dye wool a deeper shade than the cotton.*—The dyes in this group are not numerous. They are Diamine gold, Diamine scarlet B, Diamine scarlet 3B, Diamine Bordeaux S, Diamine blue RW, and Diamine green G, Diamine reds NO and B, Chicago blues G and R, Brilliant purpurine R, Diamine scarlet B, Delta purpurine 5B, Chrysamine Titan blue, Titan pink, Congo oranges G and R, Erie blue 2G, Congo R, Brilliant Congo R, Erika BN, Benzo purpurines 4B and 10B, Chrysophenine, Titan yellow, Titan browns Y, R and O, Congo brown G, Sulphon azurine B, Zambesi black B.

(4) *Dyes which produce different shades on the two fibres.*—Diamine brown G, and Diamine blue 3R, Diamine brown V, Diamine brown S, Diamine nitrazol brown B, Diamine blues BX and 3R, Diamine blue black E, Benzo blue black G, Benzo purpurine 10B, Benzo azurines R, G and 3G, Columbia red S, Brilliant azurine 5G, Titan marine blue, Congo Corinth G and B, Azo blue, Hessian violet, Titan blue, Azo mauve, Congo brown, Diamine bronze G, Zambesi browns G and 2G, Zambesi black F.

(5) *Azo-acid dyes which dye wool from neutral baths* and are therefore suitable for shading up the wool to the cotton in union fabric dyeing. Among the dyes thus available may be enumerated : Naphthol blues G and R, Naphthol blue black, Formyl violet 10 B, Lanacyl blue BB, Lanacyl

blue R, Alkaline blue, Formyl violets S4B and 6B, Rocceleine, Azo red A, Croceine AZ, Brilliant scarlet, Orange extra, Orange ENZ, Indian yellow G, Indian yellow R, Tropaeoline OO, Naphthylamine black 4B and Naphthol blue black, Brilliant scarlet G, Lanacyl violet B, Brilliant milling green B, Thiocarmine R, Formyl blue B, Naphthylamine blacks D, 4B and 6B; Azo-acid yellow, Curcumine extra, Mandarine G, Ponceau 3RB, Acid violet 6B, Guinea violet 4B, Guinea green B, Wool black 6B. As to the best methods of dyeing, that in neutral baths yields the most satisfactory results in practical working. It is done in a boiling hot or in a slightly boiling bath, with the addition of  $6\frac{1}{4}$  oz. crystallised Glauber's salt per gallon water for the first bath, and when the baths are kept standing 20 per cent. crystallised Glauber's salt, reckoned upon the weight of the goods, for each succeeding lot. In dyeing unions, the dye-baths must be as concentrated as possible, and must not contain more than from 25 to 30 times as much water as the goods weigh. In this respect it may serve as a guide that concentrated baths are best used when dyeing dark shades, while light shades can be dyed in more diluted baths. The most important factor for producing uniform dyeings is the appropriate regulation of the temperature of the dye-bath. Concerning this, the dyer must bear in mind that the direct colours possess a greater affinity for the cotton if dyed below the boiling-point, and only go on the wool when the bath is boiling, especially so the longer and more intensely the goods are boiled. The following method of dyeing is perhaps the best one: Charge the dye-bath with the requisite dyestuff and Glauber's salt, boil up, shut off the steam, enter the goods and let run for half an hour without steam, then sample. If the shade of both cotton and wool is too light add some more of the dyestuffs used for both fibres, boil up once more and boil for a quarter

to half an hour. If the wool only is too light, or its shade different from that of the cotton, add some more of the dyestuff used for shading the wool and bring them again to the boil. If, however, the cotton turns out too light, or does not correspond in shade to the wool, add some more of the dyestuffs used for dyeing the cotton, without, however, raising the temperature. Prolonged boiling is only necessary very rarely, and generally only if the goods to be dyed are difficult to penetrate, or contain qualities of wool which only with difficulty take up the dyestuff. In such cases, in making up the bath dyestuffs are to be selected some of which go only on the wool and others which go only on the cotton (those belonging to the second group). The goods can then be boiled for some time, and perfect penetration and level shades will result. If the wool takes up the dyestuff easily (as is frequently the case with goods manufactured from shoddy), and are therefore dyed too dark a shade, then dyestuffs have to be used which principally dye the cotton, and a too high temperature should be avoided. In such cases it is advisable to diminish the affinity of the wool by the addition of one-fifth of the original quantity of Glauber's salt (about  $\frac{3}{8}$  oz. per gallon water), and from three-quarters to four-fifths of the dyestuff used for the first lot. Care has to be taken that not much of the dye liquor is lost when taking out the dyed goods, otherwise the quantities of Glauber's salt and dyestuff will have to be increased proportionately. Wooden vats, such as are generally used for piece dyeing, have proved the most suitable. They are heated with direct, or, still better, with indirect steam. The method which has proved most advantageous is to let the steam run into a space separated from the vat by a perforated wall, into which space the required dyestuffs and salt are placed. The mode of working is rather influenced by the character of the goods, and the following notes will be found useful by the

union dyer. Very little difficulty will be met with in dyeing such light fabrics as Italians, cashmere, serges and similar thin textiles lightly woven from cotton warp and woollen weft. When deep shades (blacks, dark blues, browns and greens) are being dyed it is not advisable to make up the dye-bath with the whole of the dyes at once. It is much better to add these in quantities of about one-fourth at a time at intervals during the dyeing of the piece. It is found that the affinity of the wool for the dyes at the boil is so much greater than is that of the cotton that it would, if the whole of the dye were used, take up too much of the colour, and then would come up too deep in shade. Never give a strong boil with such fabrics, but keep the bath just under the boil, which results in the wool dyeing much more nearly like to cotton.

(1) *Bright Yellow*.—Use 2 lb. Thioflavine S in a bath which contains 4 lb. Glauber's salt per 10 gallons of dye liquor.

(2) *Good Yellow*.—A very fine deep shade is dyed with  $2\frac{1}{2}$  lb. Diamine gold and  $2\frac{1}{2}$  lb. Diamine fast yellow A, in the same way as the last. Here advantage is taken of the fact that while the Diamine gold dyes the wool better than the cotton, the yellow dyes the cotton the deeper shade, and between the two a uniform shade of yellow is got.

(3) *Pale Gold Yellow*.—Use a dye liquor containing 4 lb. Glauber's salt in every 10 gallons,  $2\frac{1}{2}$  lb. Diamine fast yellow A, 2 oz. Indian yellow G and  $3\frac{1}{2}$  oz. Indian yellow R. In this recipe there is used in the two last dyes purely wool yellows, which dye the wool the same tint as the fast yellow A dyes the cotton.

(4) *Bright Yellow*.—Use in the same way as the last,  $2\frac{1}{2}$  lb. Diamine fast yellow B and 3 oz. Indian yellow G.

(5) *Gold Orange*.—Use as above 2 lb. Diamine orange G,  $5\frac{1}{2}$  oz. Indian yellow R and  $1\frac{1}{2}$  oz. Orange ENZ.

(6) *Deep Orange*.—Use  $2\frac{1}{2}$  lb. Diamine orange DC,  $6\frac{1}{2}$  oz. Orange ENZ, and  $3\frac{1}{2}$  oz. Indian yellow R.

(7) *Black*.—Use 4 $\frac{1}{2}$  lb. Union black S, 2 oz. Diamine fast yellow A, 5 oz. Naphthol.

blue black and  $3\frac{1}{4}$  oz. Formyl violet S4B, with "4 lb. Glauber's salt" in each 10 gallons dye liquor. (8) *Navy Blue*.—Use  $1\frac{1}{4}$  lb. Uniqn black S, 3 lb. Diamine black BH,  $\frac{1}{2}$  oz. Naphthol blue black,  $\frac{1}{2}$  lb. Formyl violet S4B and  $2\frac{1}{2}$  oz. alkaline blue B. (9) *Red Plum*.—Use a dye bath containing  $2\frac{1}{2}$  lb. Oxydiamine violet B and  $3\frac{1}{4}$  oz. Formyl violet S4B. (10) *Dark Green*.—A fine shade can be dyed in a bath containing 3 lb. Diamine green B and  $1\frac{1}{2}$  lb. Diamine black HW. (11) *Dark Slate*.—Use 4 lb. Diamine black HW, 2 oz. Naphthol blue black and 3 oz. Azo red A. (12) *Sage*.—Use a dye-bath containing 4 lb. Diamine bronze G and  $1\frac{1}{4}$  oz. Naphthol blue black. (13) *Dark Brown*.—A fine dark shade is got from  $2\frac{1}{2}$  lb. Diamine brown V and 2 oz. Naphthol blue black. (14) *Peacock Green*.—Use  $3\frac{3}{4}$  lb. Diamine steel blue L, 13 oz. Diamine fast yellow B,  $14\frac{1}{2}$  oz. Thiocarmine R, and  $2\frac{1}{4}$  oz. Indian yellow G in a bath of 4 lb. Glauber's salt per gallon dye liquor. (15) *Dark Sea Green*.—Use 9 oz. Diamine steel blue L,  $3\frac{3}{4}$  oz. Diamine fast yellow B,  $\frac{1}{2}$  oz. Diamine orange G,  $1\frac{1}{4}$  oz. Naphthol blue black and  $\frac{3}{4}$  oz. Indian yellow G. (16) *Dark Brown*.—Use 1 lb. Diamine orange B, 1 lb. Diamine fast yellow S,  $13\frac{3}{4}$  oz. Union black S, 1 lb. Diamine brown M and  $\frac{1}{2}$  lb. Indian yellow G. Fix in an alum bath after dyeing. (17) *Dark Stone*.—Use  $\frac{1}{2}$  lb. Diamine orange B,  $3\frac{3}{4}$  oz. Union black,  $\frac{1}{4}$  oz. Diamine Bordeaux B,  $1\frac{1}{2}$  oz. Azo red A and  $\frac{3}{4}$  oz Naphthol blue black. (18) *Black*.—A very fine black can be got from  $3\frac{1}{2}$  lb. Oxydiamine black BM, 2 lb. Union black S,  $9\frac{1}{2}$  oz. Naphthol blue black and 4 oz. Formyl violet S4B. (19) *Dark Grey*.—A fine bluish shade of grey is got from 7 oz. Diamine black BH,  $2\frac{1}{4}$  oz. Diamine orange G,  $2\frac{1}{2}$  oz. Diamine orange G,  $2\frac{1}{2}$  oz. Naphthol blue black and 1 oz. Orange ENZ. (20) *Dark Blue*.—A fine shade is got by using 2 lb. Diamine black BH,  $\frac{1}{2}$  lb. Diamine black HW, and  $3\frac{1}{2}$  oz. Alkaline blue 6B. (21) *Dra&b#257;*.—Use  $3\frac{1}{2}$  oz. Diamine orange B,  $\frac{3}{4}$  oz. Union black,  $\frac{1}{8}$  oz. Diamine

Bordeaux B,  $\frac{3}{4}$  oz. Azo red A and  $\frac{1}{2}$  oz. Naphthol blue black. (22) *Plum*.—Use 2 $\frac{1}{2}$  lb. Diamine violet N, 9 $\frac{1}{2}$  oz. Union black and 1 lb. Formyl violet S4B. (23) *Bright Yellow*.—Use a dye-bath containing 4 lb. Thioflavine S, 2 lb. Naphthol yellow S, 10 lb. Glauber's salt and 2 lb. acetic acid. (24) *Pink*.—Use  $\frac{1}{2}$  oz. Diamine rose BD,  $\frac{1}{4}$  oz. Diamine scarlet B,  $\frac{1}{2}$  oz. Rhodamine B and 20 lb. Glauber's salt. (25) *Scarlet*.—A fine shade is got from 1 $\frac{1}{2}$  lb. Diamine scarlet B,  $\frac{1}{2}$  oz. Diamine red 5B and 20 lb. Glauber's salt. (26) *Orange*.—Use a dye-bath containing 3 $\frac{1}{2}$  lb. Diamine orange G, 14 $\frac{1}{2}$  oz. Tropaeoline OO, and 2 $\frac{3}{4}$  oz. Orange extra. (27) *Sky Blue*.—Use 1 $\frac{1}{2}$  oz. Diamine sky blue and 1 $\frac{1}{4}$  oz. Alkaline blue B. (28) *Bright Blue*.—A fine shade similar to that formerly known as royal blue is obtained by using 1 $\frac{1}{2}$  lb. Diamine brilliant blue G and 9 $\frac{1}{4}$  oz. Alkaline blue 6B. (29) *Maroon*.—Use 3 lb. Diamine Bordeaux B, 2 lb. Diamine violet N and 3 $\frac{1}{2}$  oz. Formyl violet S4B. (30) *Green*.—A fine green similar in shade to that used for billiard-table cloth is got from 2 lb. Diamine fast yellow B, 2 lb. Diamine steel blue L, 14 $\frac{1}{2}$  oz. Thiocarmine R and 7 $\frac{1}{4}$  oz. Indian yellow G. (31) *Gold Brown*.—A fine brown is got from 3 lb. Diamine orange B,  $\frac{1}{2}$  lb. Union black, 2 $\frac{1}{2}$  oz. Diamine brown,  $\frac{3}{4}$  oz Naphthol blue black and  $\frac{1}{2}$  lb. Indian yellow G. (32) *Navy Blue*.—Use 3 $\frac{1}{4}$  lb. Diamine black BH, 1 $\frac{1}{2}$  lb. Diamine brilliant blue G and  $\frac{1}{2}$  lb. Alkaline blue. (33) *Fawn drab*.—A fine shade is got by dyeing in a bath containing 6 $\frac{3}{4}$  oz. Diamine orange B, 1 $\frac{3}{4}$  lb. Union black,  $\frac{1}{4}$  oz. Naphthol blue black,  $\frac{1}{4}$  oz. Diamine Bordeaux B and 1 oz. Azo red A. (34) In all these colours the dye-baths contain Glauber's salt at the rate of 4 lb. per 10 gallons. (35) *Dark Brown*.—2 $\frac{1}{2}$  lb. Diamine orange B, 13 oz. Diamine Bordeaux B, 1 $\frac{1}{2}$  lb. Diamine fast yellow B, 1 $\frac{3}{4}$  lb. Union black and 3 $\frac{1}{2}$  oz. Naphthol black. (36) *Drab*.—1 $\frac{3}{4}$  lb. Diamine fast Yellow R, 3 $\frac{1}{4}$  oz. Diamine Bordeaux B, 2 $\frac{1}{2}$  oz. Union black,  $\frac{1}{2}$  oz. Naphthol blue black and 1 $\frac{1}{4}$  oz. Indian yellow G. (37).

*Dark Blue.*—Use in the dye-bath  $4\frac{1}{4}$  lb. Diamite dark blue B,  $1\frac{1}{2}$  lb. Diamine brilliant blue G,  $\frac{3}{4}$  lb. Formyl violet S 4 B and 5 oz. Naphthol blue black. (38) *Blue Black.*—Use  $3\frac{1}{2}$  lb. Union black S,  $1\frac{1}{2}$  lb. Oxydiamine black BM,  $6\frac{1}{2}$  oz. Naphthol blue black and  $\frac{1}{4}$  lb Formyl violet S4B. (39) *Dark Walnut.*— $2\frac{3}{4}$  lb. Diamine brown M,  $1\frac{1}{2}$  lb. Union black S, and  $11\frac{1}{4}$  oz. Indian yellow G. (40) *Peacock Green.*—Use in the dye-bath 3 lb. Diamine black HW,  $5\frac{1}{8}$  oz. Diamine fast yellow B,  $1\frac{1}{4}$  lb. Thiocarmine R and  $1\frac{1}{6}$  oz. Indian yellow G. (41) *Slate Blue.*—Use in the dye-bath  $6\frac{1}{2}$  oz. Diamine catechine B,  $4\frac{3}{4}$  oz. Diamine orange B,  $2\frac{1}{2}$  oz. Union black,  $2\frac{3}{4}$  oz. Orange ENZ, and  $1\frac{3}{4}$  oz. Naphthol blue black. (42) *Dark Sage.*—A good shade is dyed with 1 lb. Diamine orange B,  $6\frac{1}{2}$  oz. Union black,  $1\frac{3}{4}$  oz. Diamine brown M,  $3\frac{1}{4}$  oz. Azo red A and  $2\frac{1}{4}$  oz. Naphthol blue black. (43) *Navy Blue.*—Use 2 lb. Diamine dark blue B,  $1\frac{1}{4}$  lb. Lanacyl violet B, and 7 oz. Naphthol blue black. (44) *Bronze Green.*—A good shade is dyed with 2 lb. Diamine orange B, 5 oz. Diamine brown N,  $\frac{3}{4}$  lb. Union black S, 1 lb. Indian yellow G and  $2\frac{1}{2}$  oz. Naphthol blue black. (45) *Black.*—Use  $2\frac{1}{2}$  lb. Oxydiamine black BM and  $1\frac{1}{2}$  lb. Naphthylamine black 6 B. Another recipe,  $2\frac{1}{4}$  lb. Oxydiamine black BM, 1 lb. Diamine brown M, 1 lb. Orange ENZ and 2 oz. Naphthol blue black. (46) *Dark Brown.*—Use  $1\frac{1}{2}$  lb. Oxydiamine black BM,  $15\frac{1}{2}$  oz. Diamine brown M,  $1\frac{3}{4}$  lb. Indian yellow G and  $2\frac{3}{4}$  oz. Naphthol blue black. Another combination,  $1\frac{1}{2}$  lb. Oxydiamine black BM,  $1\frac{1}{2}$  lb. Orange ENZ, 1 lb. Indian yellow G and 5 oz. Naphthol blue black. (47) *Scarlet.*—3 lb. Benzo purpurine 4 B,  $\frac{3}{4}$  oz. Ponceau 3 RB and  $\frac{1}{2}$  lb. Curcumine S. (48) *Crimson.*— $\frac{1}{2}$  lb. Congo Corinth G, 2 lb. Benzo purpurine 10 B and  $\frac{1}{2}$  lb. Curcumine S. (49) *Bright Blue.*—2 lb. Chicago blue 6 B, 3 oz. Alkali blue 6 B,  $1\frac{1}{2}$  oz. Zambesi blue RX. After dyeing rinse and develop in a bath of 8 oz. sulphuric acid in 10 gallons of water, then rinse well. (50) *Dark Blue.*

— $2\frac{1}{2}$  lb. Columbia fast blue 2 G, 3 oz. Sulphon azurine D, 3 oz. Alkali blue 6 B. After dyeing rinse and develop in a bath of 8 oz. sulphuric acid in 20 gallons of water. (51) *Orange*.—9 oz. Congo brown G,  $1\frac{1}{2}$  lb. Mikado orange 4 RO and  $1\frac{1}{2}$  oz. Mandarine G. (52) *Dark Green*.—2 lb. Columbia green,  $\frac{1}{2}$  lb. Sulphon azurine D, 1 lb. Zambesi blue BX,  $1\frac{1}{2}$  oz. Curcumine S. (53) *Black*.—4 lb. Columbia black FB and 2 lb. Wool black 6 B. (54) *Pale Sage Green*.—5 oz. Zambesi black D,  $\frac{3}{4}$  lb. Chrysophenine G and  $1\frac{1}{2}$  lb. Curcumine S. (55) *Slate*.— $\frac{1}{2}$  lb. Zambesi black D,  $\frac{3}{4}$  oz. Zambesi blue RX,  $\frac{3}{2}$  oz. Mikado orange 4 RO and  $1\frac{1}{2}$  oz. Acid violet 6 B. (56) *Dark Grey*.—1 lb. Columbia black FB, 3 oz. Zambesi black B and  $\frac{3}{4}$  oz. Sulphon azurine D. (57) *Drab*.— $1\frac{1}{2}$  oz. Zambesi black D,  $\frac{3}{4}$  oz. Mandarine G extra,  $\frac{1}{4}$  oz. Curcumine extra and 3 oz. Mikado orange 4 RO. (58) *Brown*.—5 oz. Zambesi black D,  $\frac{3}{4}$  oz. Mandarine G extra,  $1\frac{1}{2}$  oz. orange TA and 2 oz. Mikado orange 4 RO. (59) *Nut Brown*.— $\frac{3}{4}$  lb. Congo brown G,  $\frac{1}{2}$  lb. Chicago blue RW and  $\frac{3}{4}$  lb. Mikado orange 4 RO. (60) *Dark Brown*.—1 lb. Congo brown G,  $1\frac{1}{2}$  lb. Benzo purpurine 4 B,  $1\frac{1}{2}$  lb. Zambesi black F and  $\frac{1}{2}$  lb. Wool black 6 B. (61) *Stone*.—1 oz. Zambesi black D,  $\frac{1}{4}$  oz. Mandarine G,  $\frac{1}{4}$  oz. Curcumine extra and  $1\frac{1}{2}$  oz. Mikado orange 4 RO. (62) *Slate Green*.—3 oz. Zambesi black D,  $1\frac{1}{2}$  oz. Guinea green B. (63) *Sage Brown*.— $\frac{1}{2}$  lb. Zambesi black D,  $1\frac{1}{2}$  oz. Mandarine G extra, 3 oz. Curcumine extra, 3 oz. Acid violet 6 B, 6 oz. Mikado orange 4 RO and  $4\frac{1}{2}$  oz. Curcumine S. (64) *Cornflower Blue*.—3 oz. Chicago blue 4 R,  $\frac{1}{4}$  lb. Zambesi blue RX,  $\frac{1}{4}$  lb. Acid violet 6 B and  $\frac{3}{4}$  oz. Zambesi brown G. (65) *Dark Brown*.— $1\frac{1}{2}$  lb. Brilliant orange G,  $\frac{1}{2}$  lb. Orange TA, 1 lb. Columbia black FB and  $\frac{1}{4}$  lb. Wool black 6 B. (66) *Dark Blue*.—2 lb. Chicago blue W, 1 lb. Zambesi blue RX,  $\frac{1}{2}$  lb. Columbia black FB, 10 oz. Guinea green B and  $\frac{1}{2}$  lb. Guinea violet 4 B.

## JANUS DYES IN UNION DYEING.

The Janus dyes may be used for the dyeing of half wool (union) fabrics. The best plan of working is to prepare a bath with 5 lb. zinc sulphate ; in this the goods are worked at the boil for five minutes, then the dyes dissolved in water are added, and the working continued for a quarter of an hour ; there are then added 20 lb. Glauber's salt, and the working at the boil continued for one hour, when the dye-bath will be fairly well exhausted of colour. The goods are now taken out and put into a fixing-bath of summac or tannin, in which they are treated for fifteen minutes ; to this same bath there is next added tartar emetic and 1 lb. sulphuric acid, and the working continued for a quarter of an hour, then the bath is heated to 160° F., when the goods are lifted, rinsed and dried. In the recipes the quantities of the dyes, summac or tannin and tartar emetic are given only, the other ingredients and processes are the same in all.

- (1) *Dark Blue*.— $2\frac{1}{4}$  lb. Janus dark blue B and  $\frac{1}{4}$  lb. Janus green B in the dye-bath, and 16 lb. sumac extract and 2 lb. tartar emetic in the fixing-bath.
- (2) *Blue Black*.— $3\frac{1}{2}$  lb. Janus black I and  $\frac{1}{2}$  lb. Janus black II in the dye-bath, and 16 lb. sumac extract and 2 lb. tartar emetic in the fixing-bath.
- (3) *Dark Brown*.— $2\frac{1}{2}$  lb. Janus brown B, 1 lb. Janus black I,  $3\frac{1}{2}$  oz. Janus yellow G and 5 oz. Janus red B in the dye-bath, with 16 lb. sumac extract and 2 lb. tartar emetic in the fixing-bath.
- (4) *Drab*.— $1\frac{1}{2}$  oz. Janus yellow R,  $\frac{3}{4}$  oz. Janus red B, 1 oz. Janus blue R and  $\frac{1}{4}$  oz. Janus grey BB in the dye-bath, and 4 lb. sumac extract and 1 lb. tartar emetic in the fixing-bath.
- (5) *Grey*.—5 oz. Janus blue R,  $3\frac{1}{4}$  oz. Janus grey B,  $1\frac{1}{2}$  oz. Janus yellow R and  $\frac{1}{2}$  oz. Janus red B in the dye-bath, with 4 lb. sumac extract and 1 lb. tartar emetic in the fixing-bath.
- (6) *Nut Brown*.—1 lb. Janus brown R, 8 oz. Janus yellow R and  $1\frac{1}{2}$  oz. Janus blue B in the dye-

bath, and 8 lb. sumac extract and 1 lb. tartar emetic in the fixing-bath. (7) *Walnut Brown*.—3 lb. Janus brown B, 1 lb. Janus red B, 1 lb. Janus yellow R, 1½ oz. Janus green B in the dye-bath, with 8 lb. sumac extract and 1 lb. tartar emetic in the fixing-bath. (8) *Crimson*.—2½ lb. Janus red B and 8 oz. Janus claret red B in the dye-bath, with 8 lb. sumac extract and 1 lb. tartar emetic in the fixing-bath. (9) *Dark Green*.—1½ lb. Janus green B, 1½ lb. Janus yellow R and 8 oz. Janus grey BB in the dye-bath, with 12 lb. sumac extract and 1¼ lb. tartar emetic in the fixing-bath. (10) *Chestnut Brown*.—1 lb. Janus brown R and 1 lb. Janus yellow R in the dye-bath, and 8 lb. sumac extract and 1 lb. tartar emetic in the fixing-bath.

*Cross-Dyeing*.—Before the introduction of the direct dyes the method usually followed, and indeed still used to a great extent, is that known as cross-dyeing. The goods were woven with dyed cotton threads of the required shade, and undyed woollen threads. After weaving and cleansing the woollen part of the fabric was dyed with acid dyes, such as Acid magenta, Scarlet R, Acid yellow, etc. In such methods care has to be taken that the dyes used for dyeing the cotton are such as stand acids, a by no means easy condition to fulfil at one time. Many of the direct dyes are fast to acids and, therefore, lend themselves more or less readily to cross-dyeing. For details of the dyes for cotton reference may be made to the sections on dyeing with the direct colours (chap. iv.), while information as to methods of dyeing the wool will be found in the companion volume to this on *Dyeing of Woollen fabrics*.

**Shot Effects**.—A pleasing kind of textile fabric which is now made, and is a great favourite for ladies' dress goods, is where the cotton of a mixed fabric is thrown up to form a figured design. It is possible to dye the two fibres in different colours, and so produce a variety of shot effects. These latter

are so endless that it is impossible here to enumerate all that may be produced. It will have to suffice to lay down the lines which may be followed to the best advantage, and then give some recipes to illustrate the remarks that have been made. The best plan for the production of shot effects upon union fabrics is to take advantage of the property of certain acid dyes which dye only the wool in an acid bath, and of many of the direct colours which will only dye the cotton in an alkaline bath. The process, working on these lines, becomes as follows. The wool is first dyed in an acid bath with the addition of Glauber's salt and bisulphate of soda, or sulphuric acid, the goods are then washed with water containing a little ammonia to free them from the acid, and afterwards dyed with the direct colour in an alkaline bath. Fancy or the mode shades are obtained by combining suitable dye-stuffs. If the cotton is to be dyed in light shades it is advantageous to dye on the liquor at 65° to 80° F., with the addition of 3½ oz. Glauber's salt, and from 20 to 40 grains borax per gallon water. The addition of an alkali is advisable in order to neutralise any slight quantities of acid which may have remained in the wool, and to prevent the dyestuff from dyeing the cotton too deep a shade. Very light shades can also be done on the padding machine. The dyestuffs of Group II., which have been previously enumerated do not stain the wool at all, or only very slightly, and are, therefore, the most suitable. Less bright effects can be produced by simply dyeing the goods in one bath. The wool is first dyed at the boil with the respective wool dyestuff in a neutral bath, the steam is then shut off and the cotton dyed by adding the cotton dyestuff to the bath, and dyeing without again heating. By passing the goods through cold water to which some sulphuric or acetic acid is added, the brightness of most effects is greatly increased. (1) *Gold and Green.*—First bath, 1 lb. Cyanole extra, 7½ oz. Acid green, 1½ oz.

Orange GG, and 10 lb. bisulphate of soda; work at the boil for one hour, then lift and rinse well. Second bath, 4 lb. Diamine orange G and 15 lb. Glauber's salt; work in the cold or at a lukewarm heat. Third bath, at 120° F., 4 oz. Chrysoidine and  $\frac{1}{4}$  oz. Safranine. (2) *Black and Blue*.—First bath,  $3\frac{1}{2}$  lb. Naphthol black 3 B and 10 lb. bisulphate of soda. Second bath, 2 lb. Diamine sky blue and 13 lb. Glauber's salt. Third bath,  $6\frac{1}{2}$  oz. New methylene blue N. Work as in the last recipe. (3) *Green and Claret*.—First bath,  $3\frac{1}{2}$  lb. Naphthol red C and 10 lb. bisulphate of soda. Second bath, 2 lb. Diamine sky blue FF,  $1\frac{1}{4}$  lb. Thioflavine S, and 15 lb. Glauber's salt. (4) *Gold Brown and Blue*.—First bath,  $2\frac{1}{2}$  oz. Orange ENZ,  $1\frac{1}{2}$  oz. Orange GG,  $\frac{1}{4}$  oz. Cyanole extra and 10 lb. bisulphate of soda. Second bath, 14 oz. Diamine sky blue FF and 15 lb. Glauber's salt. (5) *Dark Brown and Blue*.—First bath,  $\frac{1}{2}$  lb. orange GG,  $1\frac{1}{2}$  oz. Orange ENZ,  $1\frac{1}{2}$  oz. Cyanole extra and 10 lb. bisulphate of soda. Second bath, 12 oz. Diamine sky blue FF and 15 lb. Glauber's salt. (6) *Black and Green Blue*.—First bath, 3 lb. Orange GG, 1 lb. Brilliant cochineal 4 R, 1 lb. Fast acid green BN and 10 lb. Glauber's salt. Second bath,  $1\frac{3}{4}$  lb. Diamine sky blue FF,  $3\frac{1}{2}$  lb. Thioflavine S and 15 lb. Glauber's salt. We may here note that in all the above recipes the second bath (for dyeing the cotton) should be used cold or at lukewarm heat and as strong as possible. It is not completely exhausted of colour, only about one-half going on the fibre. If kept as a standing bath, this feature should be borne in mind, and less dyestuff used in the dyeing of the second and following lots of goods. (7) *Blue and Gold Yellow*.—3 lb. Diamine orange G, 13 oz. Naphthol blue G,  $14\frac{1}{2}$  oz. Formyl violet S4B and 15 lb. Glauber's salt. Work at just under the boil. (8) *Brown and Blue*.—1 lb. Diamine steel blue L,  $9\frac{1}{2}$  oz. Diamine sky blue, 1 lb. Orange ENZ, 1 lb. Indian yellow G,  $1\frac{3}{4}$  oz. Naphthol blue black and 15 lb.

Glauber's salt. Work at 170° to 180° F. In these two last recipes only one bath is used, all the dyes being added at once. This is possible if care be taken that dyestuffs of two kinds are used, one or more which will dye wool and not cotton from neutral baths, and those direct dyes which dye cotton better than wool. The temperature should also be kept below the boil and carefully regulated as the operation proceeds and the results begin to show themselves.

(9) *Grey and Orange*.—First bath, 3 oz. Orange extra, 1½ lb. Cyanole extra, 1 lb. Azo red A and 10 lb. bisulphate of soda. Second bath, 5 oz. Diamine orange DC and 3 oz. Diamine fast yellow B.

(10) *Green and Red*.—First bath, 2 lb. Croceine AZ, and 10 lb. Glauber's salt. Second bath, 1 lb. Diamine sky blue FF, ½ lb. Thioflavine S, and 15 lb. Glauber's salt.

(11) *Brown and Violet*.—First bath, ¾ lb. Orange extra, ¾ lb. Cyanole extra, and 10 lb. bisulphate of soda. Second bath, 5 oz. Diamine brilliant blue G, and 15 lb. Glauber's salt.

(12) *Black and Yellow*.—First bath, 7 lb. Naphthol black B, ½ lb. Fast yellow S, and 10 lb. bisulphate of soda. Second bath, 3 lb. Diamine fast yellow A, and 15 lb. Glauber's salt.

(13) *Black and Pink*.—Black as above. Pink with Diamine rose BD (see above).

(14) *Green and Buff*.—First bath, ½ lb. Orange extra, ¾ oz. Fast yellow S, and 10 lb. bisulphate of soda. Second bath, ¾ lb. Diamine sky blue FF, ½ lb. Thioflavine S, and 15 lb. Glauber's salt.

(15) *Orange and Violet*.—First bath, 9 oz. Orange extra, and 10 lb. bisulphate of soda. Second bath, ¾ lb. Diamine violet N, and 10 lb. Glauber's salt.

(16) *Black and Blue*.—First bath, Naphthol black as given above. Second bath, Diamine sky blue as given above.

(17) *Black and Yellow*.—Add first 1 lb. Wool black 6 B, and 10 lb. Glauber's salt, then, when the wool has been dyed, add 2 lb. Curcumine S to dye the cotton in the same bath.

(18) *Green and Red*.—Dye the wool by using 3 lb. Guinea green B, ¼ lb. Curcumine extra, and 10 lb.

Glauber's salt, then add to the bath  $\frac{3}{4}$  lb. Erika BN, and  $\frac{3}{4}$  lb. Congo Corinth G. (19) *Orange and Blue*.—Dye the wool first with  $1\frac{1}{2}$  lb. Mandarine G, 2 oz. Wool black 6 B, and 10 lb. Glauber's salt; then the cotton with 2 lb. Columbia blue G. (20) *Blue and Orange*.—Dye the wool first with  $\frac{3}{4}$  lb. Guinea violet B,  $\frac{3}{4}$  lb. Guinea green B, and 10 lb. Glauber's salt; then dye the cotton with 2 lb. Mikado orange 4 RO. (21) *Green and Orange*.—Dye the wool with 3 lb. Guinea green B,  $\frac{1}{4}$  lb. Curcumine extra, and 10 lb. Glauber's salt, then dye the cotton in the same bath with  $1\frac{1}{2}$  lb. Mikado orange 4 RO.

**Shot Effects by means of Sulphur Dyestuffs.**—Since sulphur colours are generally much faster to light and washing than direct cotton dyes, it is desirable to use them in dyeing cotton-wool union fabrics which are likely to suffer long exposure to the weather. But, as previously pointed out, wool is considerably deteriorated when immersed in an ordinary sulphur dye liquor, so that this presents a difficulty in the dyeing of such union fabrics in piece form. The difficulty has now, however, been largely overcome by the process devised by Lodge and Evans and more recently still by the use of protective colloids such as Protectol.

When sulphur dyes are used for shot effects in cotton-wool unions it is usual to first dye the cotton in a special sulphur dye-bath at a low temperature whereby the cotton is dyed while the wool is not affected, and then after thorough washing, dye the wool with an acid dyestuff which does not or only slightly stain the cotton. In this manner fast shot effects are obtained.

During the dyeing with acid dyes, the bath should be well acidified, since under these conditions the affinity of cotton for an acid colour is very small. Acetic acid is preferable to a mineral acid for this purpose, since mineral acids are liable to adversely affect sulphur dyestuffs.

Otherwise, dyeing with the acid dyestuff is carried out in the usual manner.

In the Lodge-Evans patented process, the sulphur dye-bath is prepared by dissolving one part of the sulphur colour with one part of sodium sulphide conc. and then adding to the solution one part of ammonium sulphate. Under these conditions, double decomposition partly occurs between the sodium sulphide and ammonium sulphate, whereby ammonium sulphide and neutral sodium sulphate are formed. Now, ammonium sulphide has no deleterious effect on wool, and the Lodge-Evens process is therefore not harmful to wool. The temperature of dyeing should be 25° to 35° C. At higher temperatures, the wool becomes appreciably dyed with the sulphur colours. With the exception of this temperature control, the dyeing is then carried out in the usual manner.

## CHAPTER VI.

### DYEING HALF SILK (COTTON-SILK, SATIN) FABRICS.

THE direct dyes of the Diamine, Benzo and Congo types have been of late years increasingly used for dyeing satin (silk and cotton), and they have quite displaced the old methods of dyeing this class of fabrics, which consisted in first dyeing the silk with an acid dye and then dyeing the cotton with a basic dye. For details of the method of applying acid dyes to silk reference made be made to Mr. G. H. Hurst's book on *Silk Dyeing*. Most of the direct colours are exceedingly well adapted for this purpose, some under certain conditions possess the property of dyeing the cotton a deeper shade than the silk, which is an advantage rather than otherwise. The dyeing of goods composed of silk and cotton is generally done in winch dye-vats, in some cases also on the jigger. •

*Method of Dyeing.*—The direct colours are as a rule dyed in a soap-bath with addition of phosphate of soda, Glauber's salt or common salt and a little soda. The addition of these salts effects a better exhaustion of the baths ; they are therefore principally used for dark and full shades, whilst pale shades are dyed with the addition of soap only or in combination with phosphate of soda. Dark or pale shades may thus be produced at will by selecting the proper additions, but the fact should not be overlooked that the greater exhaustion of the baths not only increases the depth of shade of the cotton but also causes the silk to absorb more dyestuff. Too large a proportion of salt would cause the dyestuffs to go on the fibre too quickly and thus make the dyeing liable to turn out

uneven. A large proportion of soap counteracts the effects of the salts, causing the dyestuff to go on less quickly and tending to leave the silk lighter than the cotton, in some cases even almost white, a property which is valuable in many cases, especially as enabling the silk and cotton to be dyed in different colours to obtain shot effects. It is thus obvious that a general method applicable in all cases cannot be given ; it will vary according to the effect desired, and partly also depend on the material to be dyed. The following particulars may serve as a guide for the first bath. For pale shades each 10 gallons dye-liquor should contain  $3\frac{1}{4}$  to  $6\frac{1}{2}$  oz. soap and 4 to 7 drs. soda or  $3\frac{1}{4}$  to  $6\frac{1}{2}$  oz. soap, 4 to  $5\frac{1}{2}$  drs. soda and  $3\frac{1}{4}$  to  $6\frac{1}{2}$  oz. phosphate of soda. For medium and dark shades each 10 gallons dye-liquor may contain  $3\frac{1}{4}$  to  $6\frac{1}{2}$  oz. soap, 4 to 7 drs. soda,  $3\frac{1}{4}$  to  $6\frac{1}{2}$  oz. phosphate of soda and  $6\frac{1}{2}$  to 13 oz. cryst. Glauber's salts. For two-coloured effects or dyeings, in which the silk is intended to remain as pale as possible or even white, each 10 gallons dye-liquor may contain  $4\frac{3}{4}$  to 8 oz. soap, 4 to 6 drs. soda,  $3\frac{1}{4}$  to 8 oz. phosphate of soda and  $4\frac{3}{4}$  to  $9\frac{1}{2}$  oz. cryst. Glauber's salt. The temperature of the dye-baths is generally  $175^{\circ}$  to  $195^{\circ}$  F. ; in practical dyeing it is usual to boil up the fully charged dye-bath, shut off the steam, enter the goods and dye for about three-quarters of an hour. For obtaining level dyeings in pale shades it is advisable not to enter the goods too hot, but to raise the temperature gradually. Raising the temperature, or dyeing for some time at the boil, will deepen the shade of the cotton, but at the same time will have the same effect on the silk which may sometimes be an advantage when dyeing dark shades. As a complete exhaustion of the baths does not take place, especially when dyeing dark shades, it is advantageous, nay, even imperative, to preserve the baths for further use ; they are then replenished with only about three-fourths of the quantities of dyestuffs used for the first

bath; of the soap only about one-fourth, of Glauber's salt, soda and phosphate of soda only about one-fifth, of the first quantities are necessary. The first bath should be prepared with condensed water. If none is at hand ordinary water should be boiled up with soda and soap and the scum removed. Clear soap baths are absolutely necessary for the production of pure shades and clean pieces. After dyeing, the pieces must be very well rinsed, and the colour raised or brightened with 1 pint of acetic acid in 10 gallons of water. Many of the Diamine and Titan colours being very fast to acids, but few of them will be affected by this treatment. In the following tables are given those Diamine, etc., colours especially adapted for the dyeing of goods composed of silk and cotton, divided into three groups according to their relation to silk and cotton. (1) *Dyestuffs possessing a great affinity to Cotton and tinting the Silk not at all or only very little.*—To this class belong Chicago blues, Benzo blues, Diamine fast yellow A, Diamine orange GG, Diamine orange DC, Diamine blue BB, Diamine blue, 3 B, Diamine sky blue FF, Diamine brilliant blue G, Diamineral blue R, Diamine black B, Mikado browns, Mikado oranges, Mikado yellows. (2) *Dyestuffs producing on Cotton and Silk the same or nearly the same shade but covering the Cotton better than the Silk.*—These are Thioflavine S, Diamine yellow N, Diamine gold, Diamine fast yellow B, Diamine orange B, Diamine grey G, Diamine rose BD, Diamine scarlet S, Diamine Scarlet B, Diamine scarlet 3 B, Diamine red 5 B, Diamine fast red F, Diamine Bordeaux B, Diamine Bordeaux S, Diamine violet N, Oxydiamine violet B, Diamine blue RW, Diamine black HW, Diamine steel blue L, Diamine dark blue B, Union black S, Oxydiamine black D, Diaminogene extra, Diaminogene B, Diamine brown M, Diamine brown 3 G, Diamine green B, Diamine green G. (3) *Dyestuffs producing on Cotton more or less different shades than on Silk.*

—This group comprises Diamine blue CB, Diamine blue BG, Diamine blue BX, Diamine azo blue 2 R, Diamine blue 3 R, Diamine blue black E, Diamine black RO, Oxydiamine black SOO, Diamine brown V, Diamine brown B, Diamine bronze G. Cotton brown N produces on silk darker shades than on cotton. Of course this classification cannot be taken as absolutely correct, as by raising or lowering the temperature during the dyeing process or by a larger or smaller addition of soap or Glauber's salt (common salt, phosphate of soda), the dyestuffs are more or less influenced in one or the other direction. Diamine violet N, for instance, when dyed with an increased addition of soap would dye the cotton somewhat lighter, but at the same time leave the silk perfectly white.

**Topping with Basic and Acid Dyestuffs.**—As in very few cases only the desired shade can be obtained in the first instance by bottoming with direct colours, topping generally has to be resorted to. This is best done with basic dyes, in some cases also with acid dyestuffs in cold or tepid bath with addition of sulphuric acid, hydrochloric or acetic acid. The use of acid dyestuffs is restricted to cases where the silk alone is to be shaded. In most cases basic dyestuffs are made use of, which dye silk and cotton the same shade and deepen the shade of the cotton if the latter has a sufficiently good bottom, thus giving the goods a better and fuller appearance. It is not advisable to employ basic and acid dyestuffs in the same bath except when the quantities of either class are very small. Should it be necessary to dye with large quantities of both classes, the acid dyestuffs are first dyed in a tepid acid bath and then the goods are topped with the basic dyestuffs in a fresh cold bath with the addition of a little hydrochloric or acetic acid. Of the basic dyestuffs which are available, the following are the most suitable for topping : New methylene blue N; and other brands ; New

blue D and other brands ; Cresyl blue, Methylindone B and R, Metaphenylene blue, Indazine ; the various brands of Brilliant green, Solid green and Malachite green, Capri green, Cresyl violet, Thioflavine T, New phosphine G, Tannin orange R, and the various brands of Bismarck brown ; Safranine, Magenta all brands, Tannin heliotrope, all brands of Neutral violet, Methyl violet. Of the acid dyestuffs, the following are good for topping or shading the silk : Cyanole extra, Indigo blue N, Indigo blue SGN, and the various brands of Water blue, Soluble blue, Solid blue, and Indufine ; the various brands of Acid green and Fast acid green ; Indian yellow G and R, Naphthol yellow S, Tropæoline O and OO, and the various brands of Milling yellow and Orange ; Azo red A, Azo rubine A, Archil substitute N, Azo orseille BB, Brilliant orseille C, and the various brands of Eosine, Erythrosine, Rose bengale, Rhodamine, Brilliant croceine and Brilliant scarlet ; the various brands of Formyl violet and Acid violet ; Aniline grey B and Nigrosine, soluble in water. (1) *Bright Yellow.*—Use 2 lb. Thioflavine S. (2) *Deep Orange Yellow.*—This can be dyed by using 2 lb. Diamine yellow N. (3) *Gold Yellow.*—Dye with 2 lb. Diamine gold. Some care must be taken with this, especially not to dye too hot or the silk will be dyed deeper than the cotton. (4) *Deep Orange.*—Use 2 lb. Diamine orange B. (5) *Bright Rose.*—Use 2 lb. Diamine Rose BD. Do not work too high, especially when dyeing light rose shades, as then the silk is apt to take up too much colour. (6) *Scarlet.*—Use in the dye-bath 2 lb. Diamine scarlet HS. The heat of the dye-bath should not be allowed to exceed 160° to 170° F., or there is a risk of the shades becoming somewhat duller. (7) *Crimson.*—Dye with 2 lb. Diamine fast red F. (8) *Violet.*—Use 2 lb. Oxydiamine violet B. (9) *Bright Blue.*—A fine shade is dyed with 2 lb. Diamine blue RW. (10) *Dark Green.*—Use 2 lb. Diamine black HW. This gives a fine shade of bluish green. (11)

*Gold Brown.*—Dye with 2 lb. Diamine brown 3 G at a low heat, from  $150^{\circ}$  to  $160^{\circ}$  F., otherwise the silk takes up too much colour! (12) *Dark Green.*—Dye with 2 lb. Diamine green B. (13) *Deep Rose.*—Dye with 2 lb. Diamine red 10 B. (14) *Brilliant Yellow.*—Dye with  $1\frac{1}{2}$  lb. Mikado golden yellow 8 G ; then enter into a cold bath which contains  $1\frac{1}{2}$  per cent. Auramine II. This gives a very bright shade of yellow. (15) *Dark Brown.*—Dye a bottom with 2 lb. Mikado brown 3 GO, and then top with 3 lb. Bismarek brown and  $\frac{1}{2}$  lb. Capri blue GON. (16) *Crimson.*—Dye with 2 lb. Mikado orange 5 RO and 2 lb. Hessian purple N. (17) *Sage Green.*—Dye a bottom with 2 lb. Mikado yellow G, 14 oz. Eboli green T and 3 oz. Mikado brown M, then top in a fresh cold bath with  $\frac{1}{2}$  lb. Auramine II and  $\frac{1}{2}$  oz. Acridine Orange NO. (18) *Leaf Green.*—Dye a bottom with 3 lb. Mikado golden yellow 8 G and 1 lb. Eboli blue B ; then top with  $1\frac{1}{2}$  lb. Capri green 2 G in a cold bath. (19) *Deep Brown.*—Dye with 2 lb. Mikado orange 3 RO, 3 lb. Hessian grey S and 1 lb. Hessian brown 2 BN ; then top with 7 oz. Azine green TO and  $2\frac{1}{4}$  lb. Acridine orange NO. (20) *Dark Cream.*—Bottom with 1 oz. Diamine orange G ; then top in a fresh warm bath with 1 oz. Orange GG,  $\frac{1}{2}$  oz. Indian yellow R, 5 lb. Glauber's salt and 1 lb. acetic acid. (21) *Brilliant Violet.*—Give a bottom with 1 lb. Diamine violet N ; then top in a fresh warm bath with 4 oz. Methyl violet B and 2 oz. Rhodamine. (22) *Slate.*—Bottom in a hot bath with 6 oz. Diamine dark blue B and  $1\frac{1}{2}$  oz. Diamine brown M ; then top in a fresh bath at  $170^{\circ}$  F. with 4 oz. Aniline grey B, 1 oz. Cyanole extra, 5 lb. Glauber's salt and 1 lb. acetic acid. (23) *Black Brown.*—Give a bottom with 2 lb. Cotton brown A, 1 lb. Diamine gold and  $3\frac{1}{2}$  lb. Oxydiamine black SOOO ; then top in a fresh bath at  $120^{\circ}$  F. with 4 oz. New méthylene blue N, 1 oz. Safranine and  $\frac{1}{2}$  oz. Indian yellow G. (24) *Bright Violet.*—Use  $\frac{1}{2}$  lb. Oxydiamine violet B and  $\frac{3}{4}$  oz. Diamine dark blue B ; top after

dyeing with  $\frac{1}{2}$  oz. Safranine,  $\frac{1}{4}$  oz. Methylindone B and  $\frac{1}{4}$  oz. Cyanole extra. (25) *Drab*.—Dye with 6 oz. Diamine orange G, 1 lb. Diamine bronze G and  $\frac{3}{4}$  lb Diamine brown M, topping afterwards in a bath of  $\frac{1}{4}$  oz. Aniline grey B and  $\frac{1}{4}$  oz. Bismarck brown FF. (26) *Leaf Green*.—Dye with  $\frac{1}{2}$  lb. Diamine black HW, and 1 lb. Diamine fast yellow B ; top with  $\frac{1}{4}$  oz. Brilliant green,  $\frac{1}{4}$  oz. Indian yellow R,  $\frac{1}{2}$  oz. Thioflavine T and  $\frac{1}{2}$  oz. Cyanole extra. (27) *Dark Crimson*.—Use in the dye-bath 3 lb. Diamine Bordeaux S,  $\frac{3}{4}$  lb. Diamine orange DC and  $1\frac{1}{2}$  lb. Diamine brown V, topping with 1 oz. Magenta and  $\frac{1}{2}$  oz. Formyl violet S 4 B. (28) *Turquoise Blue*—Use to dye the ground, 6 oz. Diamine sky blue FF and  $\frac{1}{2}$  oz. Diamine fast yellow A ; top with  $1\frac{1}{2}$  oz. Cyanole extra and  $\frac{1}{4}$  oz. Brilliant green. (29) *Dark Grey*.—Dye with  $\frac{1}{2}$  oz. Diamine grey G, and  $1\frac{1}{2}$  oz. Diamine brown M ; top with  $\frac{1}{4}$  oz. Orange extra and 1 oz. Cyanole extra. (30) *Brilliant Orange*.—Dye with 1 lb. Mikado orange RO, and top with 6 oz. Acridine orange NO and 12 oz. Auramine II. (31) *Brown*.—Dye a bottom colour with 3 lb. Mikado brown M, and top with 2 lb. Bismarck brown and 6 oz. Cresyl fast violet 2 RN. (32) *Deep Crimson*.—Dye with 1 lb. Columbia black R and top with 6 oz. Magenta. (33) *Pale Sea Green*.—Use in the dye-bath  $\frac{1}{2}$  oz. Chrysophenine G,  $1\frac{1}{2}$  oz. Chicago blue 6 B and  $1\frac{1}{2}$  oz. Alkali blue 6 B. (34) *Bright Crimson*.—Dye with 3 lb. Congo Corinth and top with 1 lb. Magenta. (35) *Dark Russian Green*.—Dye with 3 lb. Columbia black B ; then top with 1 lb. Malachite green. (36) *Gold Drab*.—Dye with 5 oz. Columbia black, and top with 5 oz. Chrysoidine R. (37) *Bright Olive yellow*.—Dye with  $1\frac{1}{2}$  lb. Diamine gold,  $1\frac{1}{2}$  lb. Diamine fast yellow A and  $\frac{3}{4}$  lb. Diamine bronze G ; top with  $\frac{1}{2}$  lb. Thioflavine T and  $\frac{1}{4}$  lb. Chrysoidine. (38) *Moss Brown*.—Dye with 1 oz. Diamine brown M, 6 oz. Diamine fast yellow A, 6 oz. Diamine bronze G, topping with 1 oz. new Methylene blue N and 4 oz. Orange GG. • (39) *Dark*

- Sea Green.*—Dye a bottom with 9 oz. Diamine black B and  $4\frac{1}{2}$  oz. Diamine fast yellow B, then top with 2 oz. New methylene blue M, and 2 oz. New phosphine G. (40) *Old Gold.*—Dye a ground with  $\frac{1}{2}$  lb. Diamine gold;  $1\frac{1}{4}$  lb. Diamine fast yellow A, and 6 oz. Diamine bronze G, topping with 8 oz. Thioflavine T, 1 oz. Indian yellow R and 1 oz. Brilliant green. (41) *Cornflower Blue.*—Dye the ground with  $2\frac{1}{2}$  lb. Diamine azo blue 2 B,  $1\frac{1}{2}$  oz. Alkali blue 3 B,  $\frac{1}{2}$  lb. Oxydiamine black SOOO, and top with 1 oz. Metaphenylene blue B, 2 oz. New methylene blue R and 1 oz. Indigo blue N. (42) *Slate.*—Dye with 7 oz. Diamine dark blue B and 1 oz. Diamine brown M; top with 1 oz. Aniline grey B and 1 oz. Cyanole extra. (43) *Pale Drab.*—Dye the ground with 1 oz. Diamine orange GC,  $\frac{3}{4}$  oz. Diamine bronze G and  $\frac{1}{2}$  oz. Diamine brown M; top with  $\frac{3}{4}$  oz. New methylene blue N, 1 oz. Bismarck brown and 1 oz. Cyanole extra. (44) *Deep Leaf Green.*—Dye a ground colour with  $1\frac{1}{2}$  lb. Diamine bronze G,  $1\frac{1}{2}$  lb. Diamine fast yellow A and  $1\frac{1}{2}$  lb. Diamine black HW; the topping bath is made with  $\frac{1}{2}$  lb. Brilliant green,  $\frac{1}{2}$  lb. Chrysoidine and  $\frac{1}{2}$  lb. New methylene blue N. (45) *Maroon.*—Dye with 3 lb. Diamine Bordeaux S,  $\frac{1}{2}$  lb. Diamine orange DC and  $\frac{1}{2}$  lb. Diamine brown V; top with  $\frac{1}{2}$  lb. Magenta and  $\frac{1}{2}$  lb. Formyl violet S 4 B. (46) *Heliotrope.*—Dye with 1 lb. Heliotrope 2 B. (47) *Lilac Rose.*—Dye with 8 lb. Columbia black R and 1 lb. Alkali blue B; after dyeing pass through a weak acetic acid bath, then wash well. (48) *Pea Green.*—Dye with 2 lb. Chrysophenine, 1 lb. Chicago blue 6 B and 1 lb. Alkali blue 6 B; pass, after dyeing, through a weak acetic acid bath, then wash well. (49) *Dark Drab.*—Dye with  $\frac{1}{2}$  lb. Diamine brown M, 1 lb. Diamine fast yellow A and  $\frac{3}{4}$  lb. Diamine bronze G; top with  $\frac{1}{2}$  lb. Orange GG and  $\frac{1}{2}$  lb. Cyanole extra. (50) *Deep Rose.*—Dye the bottom colour with  $\frac{1}{2}$  lb. Diamine rose BD and top with  $\frac{1}{2}$  lb. Rhodamine B and 1 oz. Safranine. (51) *Walnut Brown.*—Dye the bottom colour with 1 lb. Oxy-

diamine black D, 1 lb. Diamine brown M and 1 lb. Oxydiamine violet B ; the topping is done with 4 oz. Safranine, 2 oz. New methylene blue N and 2 oz. Chrysoidine.

**Dyeing of Plain Black.**—Diamine blacks find a very extensive application for dyeing blacks on satin, either dyed direct in one bath, or dyed, diazotised and developed. Union black S and Oxydiamine black D are particularly suitable for direct blacks, and are used either alone or in a combination with Diamine jet black SS, which produces a better covering of the silk, or with Oxydiamine black SOOO, which deepens the shade of the cotton. According to the shade required Diamine fast yellow A and B, Diamine green B or G, or Alkaline blue may be used for shading. Dye for about one hour at about 175° to 195° F. in as concentrated a bath as possible, with about 7 to 8 lb. dye per 100 lb. of satin, 8 to 16 oz. Glauber's salt and 5 to 8 oz. soap per 10 gallons dye liquor ; keep cool in the bath for some time and rinse. The raising is either done in a tepid soap bath with the addition of some new methylene blue, or in an acid bath to which Naphthol blue black, Acid green, etc., is added for shading the silk. Direct dyed blacks are especially suitable for cheap goods (ribbons, light linings, etc.), for which special fastness to water is not required ; also for tram and tussar silk pluses, which are afterwards topped with logwood. If greater fastness is required, and more especially if it is a case of replacing aniline black, Diaminogene diazotised and developed is a good dyestuff. It is extensively used for dyeing umbrella cloths and linings. Against aniline black it has the great advantage of not tendering the fibre in the least, and not turning green during storage. Diaminogene B and Diaminogene extra are mostly used for this purpose, the former for jet blacks, the latter for blue-black shades. Proceed as follows : Enter the boiled off and acidulated goods in a boiling bath as concentrated as possible, charged with 16 oz. Glauber's salt per 10

gallons liquor, and 1 lb. acetic acid per 100 lb. dry goods. For jet black add for 100 lb. satin, 6 to 8 lb. Diaminogene, 1 to 2 lb. Naphthylamine black D,  $\frac{1}{2}$  to 1 lb. Diamine fast yellow A or Diamine green B ; for very deep shades about  $\frac{1}{2}$  of the quantity of Diaminogene B may be replaced with Diamine jet black SS. For blue black, 6 to 8 lb. Diaminogene B, or 3 to 4 lb. Diaminogene B, and 3 to 4 lb. Diaminogene extra. Dye for three-quarters to one hour at the boil, allow to cool in the bath for about thirty minutes, then rinse, diazotise and develop. Phenylene diamine (93 per cent.) serves for developing jet blacks mixed with resorcin for greenish shades. Betanaphthol is used for blue blacks (1 lb. 5 oz. per 100 lb. of dry material, dissolved in its own weight of soda lye, 75° Tw.). The three developers may also be mixed with each other in any proportions. After developing soap hot with addition of new methylene blue, by choosing a reddish or a bluish brand of new methylene, blue and black may be shaded at will in the soap bath ; finally rinse and raise with acetic acid. If properly carried out this process will give a black almost equal to aniline black ; but having, as already mentioned, the advantage of not impairing the strength of the fibre, and not turning green during storage. As the dye-baths for blacks are charged with a proportionately high percentage of dyestuff for the first bath, and will not exhaust completely, it is advisable to preserve them for further use. For subsequent lots only two-thirds to three-fourths of the quantities of dyestuffs used for the first baths are required, which fact has to be taken into consideration when calculating the cost of dyeing.

**Dyeing Shot Effects on Satin.**—Not all direct colours are equally well adapted for the production of shot effects ; those enumerated in Group I. are most suitable for the purpose, and should be dyed with a larger quantity of soap than is usual for solid shades, in order to leave the silk as

little tinted as possible. Dyestuffs of the other groups may be used if the dyeing is conducted with proper care, *i.e.* keeping the baths more alkaline and lowering the temperature. The goods are dyed with the addition for the two-coloured effects previously mentioned, then they are well rinsed, and afterwards the silk is dyed with the suitable acid dyestuffs, with addition of sulphuric acid at a temperature of about 150° F. Care should be taken not to use too much acid, and to keep the temperature of the bath sufficiently low, as otherwise the acid may cause some of the dyestuff to go off the cotton and tint the silk. It is best to work at a temperature of about 150° F., with addition of about 3 oz. concentrated sulphuric acid per 10 gallons dye-liquor. For shading the silk all acid dyestuffs can be used which have been mentioned in the foregoing tables. If in shot effects the cotton is to be dyed bright and full shades, this is best achieved by dyeing with direct colours first, and then topping with basic colours as follows: Bottom the cotton first with the suitable direct colours, then dye the silk and then treat the pieces for about two hours in a cold tannin bath (about 8 oz. tannin per 10 gallons of water), then rinse once and pass through a tartar emetic bath (about 3 oz. per 10 gallons), rinse thoroughly and dye the cotton to shade with basic colours in a cold bath to which some acetic acid has been added. Should the silk become a little dull after this process, this may be remedied by a slight soaping. After dyeing rinse well and raise with acetic acid.

**Shot Effects with Black Cotton Warp.**—Effects much in favour are designs composed of black cotton and light or coloured silk. The most suitable black dye for this purpose is Diamine black BH, diazotised and developed. Dye in as concentrated a bath as possible at about 160° F. with about 6 lb. Diamine black BH, 1 lb. Diamine sky blue, pat., per 100 lb. of dry goods,  $\frac{1}{2}$  lb. Diamine orange DC, pat., with an

addition of  $6\frac{1}{2}$  oz. soap, 4 to 5 drs. soda per 10 gallons liquor, 16 qz. Glauber's salt. After dyeing rinse well in a bath containing 6 drs. soda and 3 oz. soap per 10 gallons water, diazotised in a fresh bath with 4 lb. nitrate of soda and 12 lb. hydrochloric acid (per 100 lb. of dry goods), rinse thoroughly and develop with 3 to 16 oz. metaphenylene diamine (93 per cent.), with addition of 1 to 2 lb. soda. These two operations should follow each other as quickly as possible, also care has to be taken that the diazotised goods are not exposed to direct sunlight or heat, which causes unlevel dyeings. The silk is then cleaned as far as possible by hot soaping, and dyed at about  $120^{\circ}$  to  $140^{\circ}$  F., with acid dyestuffs and the addition of sulphuric acid. After dyeing rinse as usual and brighten.

(1) *Yellow and Violet*.—Dye the cotton with 2 lb. Diamine fast yellow A, the silk with 1 lb. Cyanole extra, and 1 lb. Formyl violet S 4 B. (2) *Black and Blue*.—Dye the cotton with 5 lb. Diamine black BH, 1 lb. Diamine sky blue, and  $\frac{1}{2}$  lb. Diamine orange DC. After dyeing, diazotise and develop with metaphenylene diamine as described above. Then dye the silk with  $\frac{1}{2}$  lb. Pure soluble blue and 1 lb. Cyanole extra. (3) *Black and Crimson*.—Dye the black as in the previous recipe, then dye the silk with 2 lb. Brilliant croceine 3 B and  $\frac{1}{2}$  lb. Rhodamine S. (4) *Blue and Gold*.—Dye the cotton with 2 lb. Diamine sky blue and the silk with 1 lb. Fast yellow S. (5) *Dark Blue and Green*.—Dye the cotton with  $1\frac{1}{2}$  lb. Diamine black BH,  $1\frac{1}{2}$  lb. Diamine sky blue and  $\frac{1}{2}$  lb. Diamine azo blue 2 R; the silk with 2 lb. Naphthol yellow S and 1 lb. New methylene blue GG. (6) *Violet and Yellow*.—Dye the cotton with 2 oz. Diamine violet N and the silk with 1 lb. Fast yellow S. (7) *Orange and Violet*.—Dye the cotton with 2 lb. Diamine orange DC and the silk with 1 lb. Formyl violet S 4 B. (8) *Dark Blue and Olive*.—Dye the cotton with  $1\frac{1}{2}$  lb. Diamineral blue R and  $\frac{1}{2}$  lb. Diamine

azobase blue 2 R, and the silk with 1 lb. Naphthol yellow S. and 1 lb. Orange GG. (9) *Green and Pink*.—Dye the cotton with 1½ lb. Diamine fast yellow A and ¼ lb. Diamine sky blue, and the silk with 1 lb. Erythrosine B. (10) *Brown and Blue*.—Dye the cotton with 3 lb. Mikado brown 2 B, and the silk with ½ lb. Pure blue. It is quite possible to produce two-coloured effects containing blue in one bath by using Alkali blue as a constituent with a direct dye which works only on to the cotton, the Alkali blue going on to the silk, as, for example, in the following recipes :—

(11) *Orange and Blue*.—The dye-bath is made with 3 lb. Mikado orange 5 RO and 1¼ lb. Alkali blue 6 B. After the dyeing the goods are rinsed, then passed through a bath of 1½ lb. sulphuric acid in 10 gallons water, washed well, and dried.

(12) *Olive and Blue*.—The dye-bath is made with 1½ lb. Diamine fast yellow A, 2½ lb. Diamine orange DC, ¼ lb. Diamine sky blue, and 1 lb. Alkali blue 6 B. After dyeing rinse, then acidulate as above and wash well.

## CHAPTER VII.

### THE DYEING OF ARTIFICIAL SILK.

THE dyeing of artificial silk, though requiring care and experience, has now become of considerable importance, and it may be noted that in 1924 nearly twice as much artificial silk was produced as the natural variety. In the future, there is every possibility that the production of artificial silks will continue to increase.

At the present time there are four chief varieties of artificial silk being produced—Chardonnet, cuprammonium, viscose and cellulose acetate (Celanese and Lustron) silks. All of these are made from cellulose, and with the exception of cellulose acetate silk consist of pure cellulose. Consequently, the dyeing properties of Chardonnet silk, cuprammonium and viscose silks are similar to those of cotton, with a few exceptions. On the other hand, since cellulose acetate is an ester of cellulose, its dyeing properties are quite different from those of cotton, so that it may almost be considered as a distinct fibre.

All artificial silks are valued because of their lustre, so that during dyeing care must be taken to avoid loss of lustre. To this end, dyeing is usually carried out in soap baths, and in the case of cellulose acetate silks is not carried out at temperatures exceeding 75° to 80° C., and after dyeing, the silk is usually treated with a solution of soap before being finally rinsed and dried.

Furthermore, since Chardonnet, cuprammonium and viscose silks have a greater affinity than that of cotton

for most dyestuffs, they tend to dye unevenly. Artificial silks resemble mercerised cotton in this respect and therefore the usual precautions, are necessary to prevent the colour rushing on to the fibre.

The chief factors concerning the dyeing of each type of artificial silk will now be noted.

*Chardonnet Silk.*—This fibre, being produced from a nitrated cellulose always contains some nitrogen, even though it is denitrated in one stage of its manufacture. The nitrogen is combined with the cellulose in such a manner as to give Chardonnet silk increased acidic properties. Hence this silk has a considerable affinity for basic dyestuffs. It thus differs from cotton. On the other hand, it has a strong affinity for all the dyes which are usually applied to cotton, so that its dyeing may be carried out as with cotton. It should be noted, however, that Chardonnet silk has a slightly decreased affinity for many direct dyestuffs.

*Cuprammonium Silk.*—This consists of regenerated cellulose and is therefore dyed as for viscose silk.

*Viscose Silk.*—In England, viscose silk is almost entirely produced by Messrs. Courtaulds, Ltd., of Coventry, and their many years' experience in its manufacture enables them now to produce a very satisfactory and uniform article.

Before dyeing, the silk should be wetted-out in a soap liquor at 40° to 50° C. containing about 2 parts of soap per 1000 parts of water, to which it is preferable to add 2 parts of .880 ammonia, and after rinsing in soft water the silk is then ready for dyeing. This soap-treatment before dyeing is usually the only one required since nearly all the viscose silk met with by dyers is in the bleached condition. However, when bleaching is necessary it may be carried out as for cotton, using solutions of sodium hypochlorite or bleaching powder.

Dyeing is carried out at all temperatures up to 95° C. A temperature of 95° C. is preferable. The dyeing is carried out as for mercerised cotton. Viscose silk has a greater affinity than cotton for basic dyestuffs, so that these may sometimes be used for shading purposes. Otherwise viscose silk may be dyed with all the usual dyestuffs used for cotton.

It will here be noted, however, that variations in the conditions of manufacture considerably affect the affinity of viscose silk for various dyestuffs. Though these variations are reduced to a minimum by a strict scientific control over every stage in the manufacture, yet a certain lack of uniformity exists among viscose silks. It is found, however, that such variations in the affinity of viscose dyes is more apparent with certain dyes than with others—a difference which is related to the chemical constitution of the individual dyestuffs. Hence Messrs. Courtaulds have classified most dyestuffs according to whether they dye viscose silk evenly or unevenly; and by their courtesy, the following classification is included here. Further, it is to be noted that the classification of a dyestuff as uneven does not imply that this dyestuff cannot be successfully used—all that is implied is that a variation in the quality of the silk will be revealed if such variation exists.

### Direct Cotton Dyestuffs.

#### *Even Dyes.*

Benzo fast black L.

, " , Bordeaux 6 BL.

, " , heliotrope, BL, 2 RL.

, " pürpurine 4 B.

Brilliant benzo fast yellow GL.

, " Chlorantine fast Bordeaux 2 RL.

**Chlorantine fast violet BL, 4 BL.**

    ,,     ,,     yellow 4 GL.

**Chlorazol black SD.**

    ,,     brown G.

    ,,     fast black BK.

    ,,     ,,     Bordeaux LK.

    ,,     ,,     helio BK.

    ,,     ,,     red FG, K, A.

**Chrysophenine G.**

**Congo orange R.**

**Diamine aldehyde Bordeaux B.**

    ,,     azo fast green G.

    ,,     fast red F.

    ,,     yellow N.

**Diaminogene extra.**

    ,,     sky blue N.

**Diazo brilliant orange 5 G extra.**

    ,,     ,,     ,,     GR     ,,

    ,,     fast scarlet B, BA.

    ,,     ,,     violet BL.

    ,,     ,,     yellow G, 2 G.

    ,,     indigo blue 4 GL extra.

    ,,     ,,     ,,     3 RL.

    ,,     rubine B.

    ,,     geranine B extra.

    ,,     sky blue 3 GL extra.

**Direct catechine GR.**

    ,,     fast black B.

    ,,     ,,     orange SE.

    ,,     ,,     violet 2 B.

**Naphthamine fast grey B.**

**Naphthogene pure blue 4 G.**

**Neutral grey G.**

**Oxamine red.**

Paramine brown B.  
 ,,, fast red F.  
 Pritnuline.  
 Pyrazole orange G, R, 2 R.  
 Triazogene orange R.  
 Triazol fast yellow 2 G.  
 Zambesi black D.

*Moderately Even Dyes.*

Benzo fast heliotrope 4 BL.  
 ,,, chrome brown G.  
 ,,, purpurine 10 B.  
 Chlorazol black DV.  
 ,,, catechine GR.  
 ,,, dark green PL.  
 ,,, fast yellow B.  
 Diamine catechine G.  
 ,,, fast brown GB.  
 ,,, ,,, yellow B.  
 Diazamine blue BR.  
 Diazo brown 3 G.  
 ,,, fast blue 4 GW.  
 Naphthamine light violet 2 B.  
 Oxyphenine 2 G, R.  
 Stilbene orange 4 R'

*Uneven Dyes.*

All direct cotton blues, including both those of good and moderate fastness to light.

Benzo fast eosine BL.  
 ,,, ,,, orange 2 RL.  
 ,,, ,,, scarlet 4 BS.  
 Benzoform green FFL.

Chlorantine fast brown 2 GL, RLZ

Chlorazol black BH.

„ „ E extra	In grey and slate shades.
„ „ LF.	

Direct deep black EW.

Diamine black BH.

Chlorazol brown 2 G, GM, M, and PB.

„ drab RH.
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„ fast brown BK.
------------------

„ orange AG and G.
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„ cosine B.
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„ pink BK.
------------

„ scarlet 4 BS.
-----------------

Chromanil brown 2 G.

Congo rubine.

Diamine catechine 3 G.

„ fast brown G.
-----------------

„ „ orange EG and ER.
-----------------------

Diazo brilliant green 3 G.

„ fast blue GW, 2 BW.
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„ „ green BL.
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Formic black C.

Trisulphon drab RH.

„ bronze G.
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When using direct cotton dyestuffs for the dyeing of viscose it should be remembered that :—

(1) The higher the temperature of the dye-bath, the more even is the result.

(2) Dyeing in a simple soap bath gives the most even results with those dyestuffs which have an affinity for viscose, without the use of Glauber's salt.

(3) The use of Glauber's or common salt increases the liability to uneven results, so that their use should be kept down to a minimum.

(4) When dyeing compound shades, dyestuffs possessing the same degree of uneven dyeing properties should be used as far as possible : it is not wise to mix a dyestuff classified as "even dyeing" with one of "uneven dyeing" properties, if it can be avoided.

### Basic Dyestuffs.

Experience has shown that basic dyestuffs in general give more even results on viscose mordanted with Katanol than when mordanted with Tannic acid. The following list gives the results obtained both on Katanol and Tannic acid mordants with various dyestuffs.

	Katanol Mordant.	Tannin Mordant.
Acridine yellow G . . .	Fair.	Fair.
Citroflavine 6 G . . .	Good.	Fairly good.
Rhoduline yellow 6 G, T . . .	„ „	Good.
Acronol yellow T . . .	„ „	Fairly good.
Auramine O . . .	Fairly good.	Poor.
„ G . . .	Good.	Good.
Methylene blue ZF . . .	„ „	Poor.
Cresyl blue 2 BS . . .	Poor.	Good.
Torquoise blue 2 B . . .	Good.	Poor.
Methylene blue 2 B . . .	Poor.	„
Brilliant Rhoduline blue R . . .	„ „	„
Acronol brilliant blue . . .	„ „	Very poor.
Torquoise blue G . . .	Good.	Poor.
Setoglaucine . . .	Fair.	Fair.
Rhoduline blue GG and 5 B . . .	Good.	„
„ sky blue 3 G . . .	„ „	Good.
„ blue 3 GC ..	Fair.	Poor.
Malachite green crystals A . . .	„ „	„
Rhoduline sky blue 2 B . . .	„ „	Fair.
Rhodamine 6 G . . .	Fairly good	Poor.

Rhoduline orange RC.	Good.	Good.
Brilliant Rhoduline purple R.	Poor.	Poor.
Rhoduline orange N	"	Fairly good.
Rhodamine-B	"	Good.
Rhoduline red B and G	Good.	Fair.
Bismarck brown	Fair.	Poor.
Chrysoidine YRP	"	"
Brilliant Rhoduline red B	"	Fair.
Rhoduline heliotrope 3B	"	Good.
Magenta crystals	Poor.	Poor.
Methyl violet 2 B	"	"
" " 10 BL	"	"
Brilliant Saffranine BR and G	Good.	Fair.
Thionine blue GO	"	Poor.

### Sulphur Dyestuffs.

The sulphur dyestuffs, almost without exception, give uneven results on viscose and their use should therefore be avoided unless the fastness required demands their employment.

The use of Sulphur blacks for black shades is permissible.

### Vat Dyestuffs.

#### *Even.*

Algole blue 3 R.	
,, brilliant orange FR.	
,,     ,, red 2 B.	
,,     ,, violet 2 B and R.	
,, pink R.	
,, yellow R.	
Caledon red BN	
Indanthrene red BN.	
Duranthrene red BN.	

- .. pink B.
- .. heliotrope B.
- .. red G.
- .. violet B and R.

Cibanone brown V.

- .. green B.
- .. olive B.
- .. yellow R.

Duranthrene Bordeaux R.

- .. brilliant violet R.
- .. claret B.
- .. golden orange Y.
- .. red B.

Hydranthrene violet B.

Hydron Bordeaux B.

- .. brown G.
- .. green R

#### VIOLET D.

Indanthrene brown 3 R.

- .. golden orange G, RN and 3 R
- .. grey B and 3 B.
- .. pink B.
- .. violet RR.

*Moderately Even.*

Algole Corinth R.

- .. olive R.

Daranthrene red 5 G.Y.

„ „ violet 2 RN.

Algole red FF.

Anthraflavone.

Caledon grey KT.

„ jade green.

Duranthrene yellow G.

Hydron Bordeaux R.

„ green G.

Indanthrene golden orange R.R.T.

„ red violet 2 RN.

#### *Uneven.*

Algole blue K.

„ brown G and R.

„ grey 2 B.

Cibranone orange R.

Hydron blue G and R.

„ brown OG and R.

„ navy blue C.

Indanthrene black 2 B.

Hydranthrene black 2 B.

Caledon black 2 B.

„ green B.

*Cellulose Acetate (Celanese or Lustron) Silk.*—As previously indicated, the silk differs from other silk substitutes in that it consists not of pure cellulose but of a cellulose ester. From its content of acetyl groups, the cellulose acetate silk now being manufactured contains two to three  $\text{CH}_3\text{CO}$  groups per  $\text{C}_6\text{H}_{10}\text{O}_5$ .

Cellulose acetate silk is not wetted out so easily as other silks, but the simple soap treatment, as described for viscose silk, is sufficient to prepare it for dyeing. On the

other hand, cellulose acetate silk is more susceptible to alkalis than the other silks, since being an ester, it is easily saponified. The use of a caustic alkali in the dye-bath is therefore undesirable. Further, cellulose acetate silk is soluble in organic solvents, and in water it should not be heated above 75° to 80° C.

The dyeing properties of cellulose acetate are an important feature of the silk, since they are quite different from those of cotton, Chardonnet, cuprammonium and viscose silks. In fact, the difficulties of dyeing it seriously restricted its application in the textile industry. Owing to the discovery of the S.R.A. colours by G. H. Ellis these difficulties have now been overcome and it is now possible to dye this silk by simple methods and obtain pleasing and satisfactory shades.

Early in the manufacture of cellulose acetate silk it was discovered that this silk had no affinity for ordinary direct dyestuffs, though it had a strong affinity for most basic dyes. For instance, when a cotton—cellulose acetate union fabric is dyed by means of Benzopurpurine 4 B, the cotton is dyed a bright red, while the cellulose acetate remains perfectly white and unstained. On the other hand, cellulose acetate can be dyed directly with Malachite green, Bismarck brown, Rhodyline 4 G and Méthyl violet 2 B, yielding shades which are of reasonable fastness. Owing, however, to the fugitive character of basic dyes and the discovery of better substitutes, they are not now used in dyeing cellulose acetate silk, except for topping purposes.

Generally, it is found that direct dyestuffs which contain sulphonic acid groups are not suitable for dyeing cellulose acetate silk, since they have no affinity for it. Similarly, Stilbene dyestuffs such as Cotton yellow CH and also vat and sulphur dyestuffs are unsuitable for cellulose acetate. Dyestuffs of large molecular complexity have but little

affinity for cellulose acetate, and among these may be classed the triazo colouring matters.

On the other hand, certain acid and chrome colours possess a useful affinity for cellulose acetate. Among these may be mentioned Alizadin brown.

The following is a list of dyes which were early found suitable for dyeing cellulose acetate silk directly and they are still in use :—

Cellutyl fast yellow A.Y.

„ „ „	C.
„ „ golden yellow.	
„ „ yellow AB.	
„ „ orange R.	
„ „ „ GK.	
„ „ „ G.	
„ orange 2 R.	
„ fast tangerine	
„ „ red D.	
„ bright red.	
„ fast lilac.	
„ „ blue.	
„ sky blue.	
„ fast bright green B.	
„ „ „ „ Y.	
„ grey.	

It is not necessary to mordant cellulose acetate silk with tannic acid when basic dyes are used ; in fact tannic acid has practically no affinity for this silk.

It will here be necessary to mention a method for dyeing cellulose acetate silk which is useful but is now almost entirely superseded by other methods. In this method, the silk is superficially saponified before dyeing, so that the silk then has an outer layer of regenerated cellulose and so can be dyed by the usual methods employed for

cotton and other artificial silks. This saponification is not desirable since it reduces somewhat the valuable water-repellant properties of the silk.

The usual method of treatment consists of soaping the cellulose acetate silk in the manner previously described and then working it for  $\frac{1}{4}$  hour in a bath at 75° C. containing 100 gallons of water and 3 lb. of 72° Tw. caustic soda for every 10 lb. of silk. It is afterwards washed in warm water, soured with acetic acid, again washed and then lightly soaped.

This partially saponified silk may then be dyed with the usual direct and sulphur dyestuffs, including those named below.

**Chlorazol fast yellow NX.**

- „ „ orange D.
- „ „ red K.
- „ violet N.
- „ fast blue 2 B.
- „ sky blue GW.
- „ green BN.
- „ dark green PL.
- „ brown M.
- „ black E extra.
- „ black BH.

**Cross dye yellow Y.**

**Chlorazol fast yellow E.**

- „ „ red FG 9202 K.

**Thionol Corinth RBX.**

- „ „ blue 2 B.

**Cross dye sky blue FFS.**

- „ „ green 2 G conc.

- „ „ brown 2 R.

**Thionol black brown R 9146 K.**

- „ „ „ XXN conc.

- „ „ „ OG.

**Cross dye black BX.**

Later, new dyestuffs—Ionamines—were discovered by A. G. Green, and these at the time of their discovery represented an important advance in the dyeing of cellulose acetate silk. Since that time, however, they have lost much of their importance. The following Ionamine dyes are available :—

Ionamine A (yellow).		Ionamine MA (golden yellow).	
„	B (orange).	„	KA (red).
„	H (yellow).	„	GA (terra-cotta red).
„	L (yellow).	„	blue R (fluorescent blue).
Ionamine blue G (pure blue).			

Generally these colours have good fastness to washing and perspiration, and they are capable of being diazotised and developed by means of beta-naphthol, resorcine and beta-oxynaphthoic acid. The following table indicates the range of shades obtainable with four of these dyes on development :—

Method of Dyeing.	Ionamine A	Ionamine B	Ionamine H.	Iofamine L Paste.
Direct	Yellow.	Orange.	Yellow.	Yellow.
Developed with beta-naphthol	Not suitable.	Scarlet.	Bluish-Red.	Blue-Violet.
Resorcine	Not suitable.	*Orange Brown.	Not suitable.	Reddish-Brown.
Beta-oxynaphthoic acid	Black.	† Red.	Not suitable.	Blue.

The chemical constitution of the Ionamines is somewhat peculiar.

The principles underlying their application is based on the fact that cellulose acetate silk has a strong affinity for aromatic compounds containing amino groups. Such compounds are usually insoluble in water and therefore of little use in dyeing. However, by means of formaldehyde and

\* Fastness to washing only fair.

† Fastness to washing only good.

sodium bisulphite they can be converted into soluble bodies, which readily hydrolyse in aqueous acid or alkaline solutions, and the Ionamines are of this type.

Hence in dyeing with an Ionamine dyestuff, the dye liquor is made acid, preferably with formic acid. During dyeing, the Ionamine decomposes, thereby liberating the insoluble dyestuff of which it partly consists, and simultaneously, this insoluble dye is not precipitated in the liquor, but is absorbed by the cellulose acetate silk. Obviously, the dyeing must be stopped immediately the desired depth of shade is obtained.

The general procedure for dyeing with Ionamines is as follows :—

The silk material should be well wetted out at 50° C. in a bath containing 2 lb. of soap and 2 pints of .880 ammonia per 100 gallons of liquor, and then entered in the luke-warm dye-bath containing 1 to 3 per cent. of the dyestuff and 1 per cent. of formic acid. During the next  $\frac{1}{2}$  hour the bath should be heated to 75° C. and maintained at this temperature for about  $\frac{3}{4}$  hour, when the dyeing will be about complete.

For Ionamines B and H, 2 per cent. of formic acid should be used. In place of formic acid, one quarter and one half the amount of sulphuric or hydrochloric acids respectively may be used.

After dyeing, the silk material should be rinsed in a solution made slightly alkaline by means of ammonia or sodium carbonate and afterwards lightly soaped, rinsed and dried. If, however, the dyed material is to be subsequently developed, it should merely be rinsed in cold water and then treated for about twenty minutes in a cold diazotising bath containing 5 per cent. of sodium nitrate and 10 per cent. of hydrochloric acid of 32° Tw. It should then be rinsed and immersed for about  $\frac{1}{2}$  hour in a developing bath containing

6 per cent. of the developer. When the full shade is developed, the dyed material is rinsed and lightly soaped in a  $\frac{1}{4}$  per cent. solution of soap at about  $40^{\circ}$  to  $50^{\circ}$  C.

An important point in confection with the dyeing of artificial silks is that every care must be taken to preserve their pleasing lustre. This can only be done by avoiding the use of temperatures higher than  $75^{\circ}$  to  $80^{\circ}$  C. and by handling the silk material carefully.

Several anthraquinone products, chiefly the amino-anthraquinones, have been found to have a useful affinity for cellulose acetate silk when applied as in aqueous suspension. Thus Messrs. Scottish Dyes, Ltd., have made available the following Celatene dyes :—

Celatene yellow.

,, orange.

,, red.

,, , violet.

,, black.

,, blue.

Though yielding fast shades they are expensive.

The most important dyes for cellulose acetate silk are those termed S.R.A. colours. These have been developed by Messrs. British Celanese, Ltd., and essentially consist of suitable azo and anthraquinone dyes dissolved in sulphonated fatty oils. It was discovered that many dyes having a good affinity for cellulose acetate silk were insoluble in water so that their application was difficult. When, however, it was found that such substances could be dissolved in Turkey red oil and that dilution of this solution yielded a stable colloidal solution of the dyestuff, it became possible to prepare dye pastes suitable for dyeing cellulose acetate silk. The S.R.A. dyes were developed on these lines. They are usually viscous pastes and yield clear aqueous solutions when diluted.

The application of S.R.A. dyes to cellulose acetate silk is therefore very simple. The S.R.A. dye is first dissolved in a small quantity of hot (preferably not boiling) soft water and then added to the dye-bath. Since these dyes contain fatty acids, the dye-bath must be maintained slightly alkaline by addition of ammonia so as to avoid the formation of a fatty acid scum. Dyeing is carried out by immersing the cellulose acetate silk in the dye liquor at a temperature not exceeding about 75° C. until the desired shade is obtained and the dyed silk is then well washed with warm water.

The shades obtainable with S.R.A. dyes are of excellent all-round fastness and in some cases almost equal the basic dyes in brightness.

At present the following S.R.A. dyes are available :—

S.R.A. pure yellow I.

“ “ “ II.

“ golden yellow VIII.

“ “ “ IX.

“ orange I.

“ “ II.

“ red I.

“ “ III.

“ “ V.

“ heliotrope I.

“ violet II.

“ blue III.

“ “ IV.

“ “ V.

“ black III. (this is developed with oxynaphthoic acid).

*Dyeing of Mixed Artificial Silk Materials.*—Advantage is now being taken of the different dyeing properties of cellulose acetate silk and viscose, Cuprammonium and

Chardonnet silks, chiefly in the production of two-colour effects. Thus, whereas cellulose acetate silk has no affinity for direct dyestuffs, the other three artificial silks have, and also while cellulose acetate has a good affinity for Ionamine and S.R.A. dyes, the other silks have not. Moreover, viscose and cuprammonium silks have but little affinity for several of the Cellutyl dyes, *e.g.*, Cellutyl yellow C. Hence, when a union fabric, composed of, say, cellulose acetate and viscose silk is dyed in a bath containing Chlorazol sky blue FF and Cellutyl yellow C, the resulting dyed fabric contains yellow cellulose acetate and blue viscose silk—a pleasing shot effect. This method of dyeing, therefore, allows of shot effects being dyed in one bath—a very economical procedure, and one which allows very varied effects to be obtained.

## CHAPTER VIII.

### OPERATIONS FOLLOWING DYEING.

*Washing, Soaping, Drying.*—After loose cotton or wool, or cotton and woollen yarns, or piece goods of every description have been dyed, before they can be sent out for sale they have to pass through various operations of a purifying character. There are some operations through which cloths pass that have as their object the imparting of a certain appearance and texture to them, generally known as finishing processes ; of these it is not intended here to speak, but only of those which precede these, but following on the dyeing operations. These processes are usually of a very simple character, and common to most colours which are dyed, and here will be noticed the appliances and manipulation necessary in the carrying out of these operations.

**Squeezing or Wringing.**—It is advisable when the goods are taken out of the dye-bath to squeeze or wring them according to circumstances, in order to press out all surplus dye-liquor, which can be returned to the dye-bath if needful to be used again. This is an economical proceeding in many cases, especially in working with many of the old tannin materials like sumac, divi-divi, myrobolams, and the modern direct dyes which in the dyeing operations are not completely extracted out of the bath, or in other words, the dye-bath is not exhausted of colouring matter, and, therefore, it can be used again for another lot of goods, simply by adding fresh material to make up for that absorbed by the first lot of goods. Loose wool and loose

cotton are somewhat difficult to deal with by squeezing or wringing, but the material may be passed through a pair of squeezing rollers, such as are shown in Fig. 38, which will be more fully dealt with later on.

*Yarns in Hanks.*—In the hank-dyeing process the hanks are wrung by placing one end of the hank on a wringing

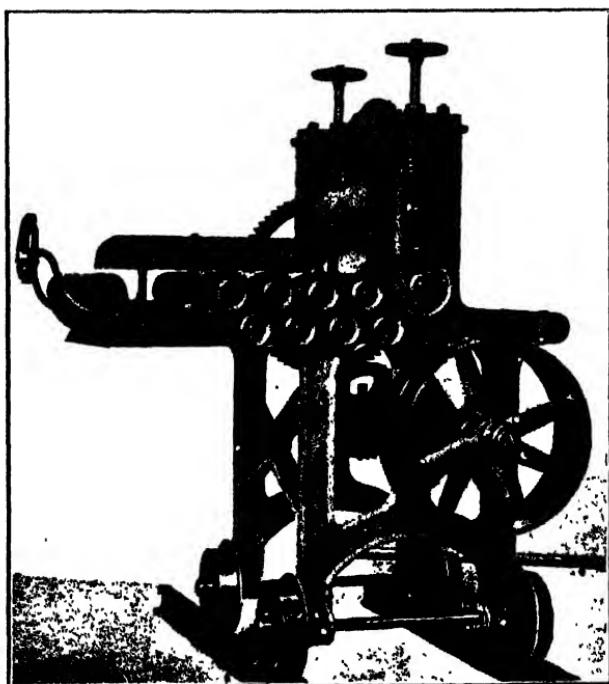


FIG. 38. Squeezing rollers.

horse placed over the dye-tub, a dye stick on the other end of the hank giving two or three sharp pulls to straighten out the yarn, and then twisting the stick round ; the twisting of the yarn puts some pressure on the fibres, thoroughly and uniformly squeezing out the surplus liquor from the yarn.

*Hank-wringing Machines.*—Several forms of hank-wringing machines have been devised. One machine consists of

a pair of discs fitted on an axle ; these discs carry strong hooks on which the hanks are placed. The operator places a hank on a pair of the hooks. The discs revolve and carry round the hank ; during the revolution the hank is twisted and the surplus liquor wrung out ; when the revolution of the disc carries the hank to the spot where it entered the machine the hooks fly back to their original position, the hank unwinds, it is then removed and a new hank put in its place, and so the machine works on, hanks being put on and off as required. The capacity of such a machine is great, and the efficiency of its working good. Mr. S. Spencer of Whitefield makes a hank-wringing machine which consists of a pair of hooks placed over a vat. One of the hooks is fixed, the other is made to rotate. A hank hung between the hooks is naturally twisted, and all the surplus liquor wrung out, the liquor falling into the vat.

*Roller Squeezing Machines for Yarn.*—Hanks may be passed through a pair of india-rubber squeezing rollers, which may be so arranged that they can be fixed as required on the dye-bath. Such a pair of rollers is a familiar article, and quite common and in general use in dye houses.

*Piece Goods.*—These are generally passed open through a pair of squeezing rollers which are often attached to the dye-vat in which the pieces are dyed.

**Washing.**—One of the most important operations following that of dyeing is the washing with water to free the goods, whether cotton or woollen, from all traces of loose dye, acids, mordanting materials, etc., which it is not desirable should be left in, as they might interfere with the subsequent finishing operations. For this purpose a plentiful supply of good, clean water is required ; this should be as soft as possible, free from any suspended matter which might settle upon the dyed goods, and stain or speck them. Washing may be done by hand, as it frequently was in olden

days, by simply immersing the dyed fabrics in a tub of water, shaking, then wringing out, again placing in fresh water to finish off. Or if the dye-works were on the banks of a running stream of clean water the dyed goods were simply hung in the stream to be washed in a very effectual manner. In these days it is best to resort to washing machines adapted to deal with the various kinds of fibrous materials and fabrics in which they can be subjected to a current of water.

*Loose Wool and Cotton.*—If this has been dyed by hand, then the washing may also be done in the same way by hand in a plain vat. If the dyeing has been done on a machine, then the washing can be done on the same machine.

*Yarns.*—Yarn in the cop form is best washed in the machine in which it is dyed.

*Yarns in Hanks.*—A very common form of washing machine is shown in Fig. 39. As will be seen it consists of a wooden vat, over which are arranged a series of revolving reels on which the hanks are hung. The hanks are kept in motion through the water, and so every part of the yarn is thoroughly washed. Guides keep the hanks of yarn separate and prevent any entanglement one with another. A pipe delivers constantly a current of clean water, while another pipe carries away the used water. Motion is given to the reels in this case by a donkey engine attached to the machine, but it may also be driven by a belt from the main driving shaft of the works. This machine is very effective.

*Piece Goods.*—Piece goods are mostly washed in machines, of which two broad types may be recognised; first, those where the pieces are dealt with in the form of ropes in a twisted form, and, second, those where the pieces are washed open.

A machine for washing fabrics in rope form is illustrated in Fig. 40.

It contains a pair of rollers whose purpose is to draw the

THE DYEING OF COTTON FABRICS

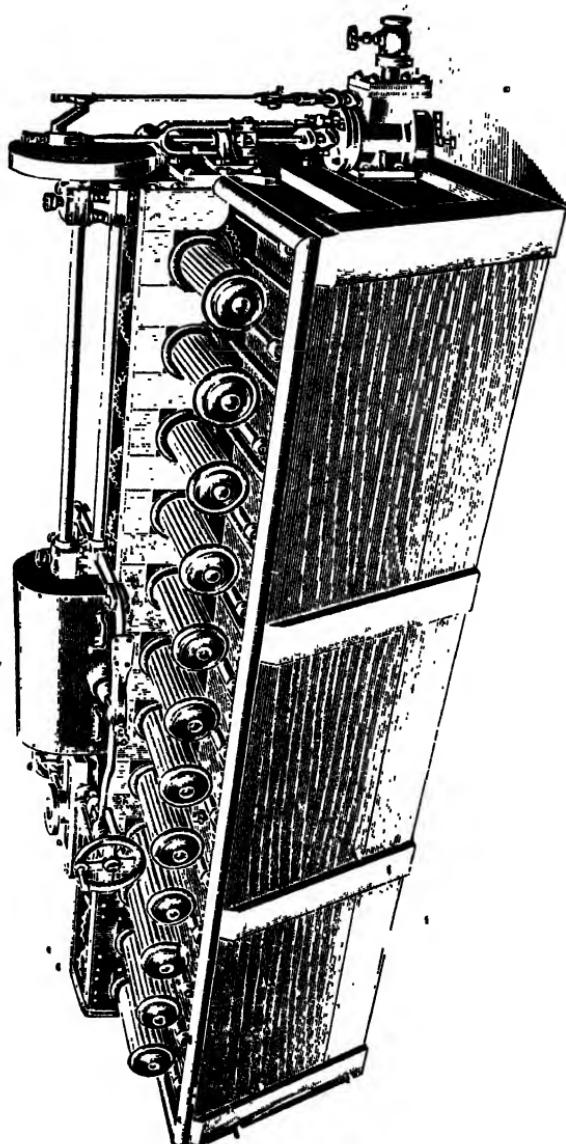


FIG. 39.—Yarn-washing machine.

cloth through the machine and also partly to act as squeezing rollers. The cloth is threaded in rope form spirally round the rollers, passing in at one end and out at the other, pegs in a guide rail serving to keep the various portions separate.

Fig. 41 shows a washing machine very largely used in the wool-dyeing trade. The principal portion of this machine is of wood. The internal parts consist of a large wooden bowl, or oftener, as in the machine under notice, of a pair of wooden bowls which are pressed together by springs with some small

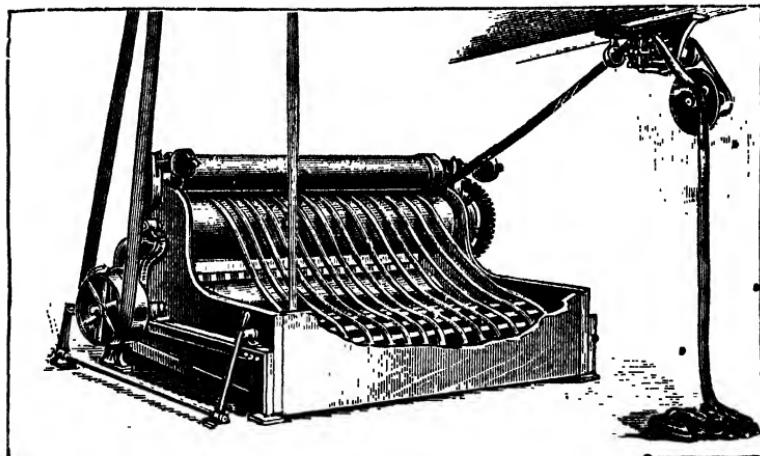


FIG. 40.—Dye-house washing machine.

degree of force. Between these bowls the cloth is placed, more or less loosely twisted up in a rope form, and the machines are made to take four, six, or eight pieces, or lengths of pieces, at one time, the ends of the pieces being stitched together. A pipe running along the front of the machine conveys a constant current of clean water which is caused to impinge in the form of jets on the pieces of cloth as they run through the machine, while an overflow carries away the used water. The goods are run in this machine until they are considered to be sufficiently washed, which may take

half to one and a half hours. In Fig. 42 is shown a machine designed to wash pieces in the broad or open state. The machine contains a large number of guide rollers, built more

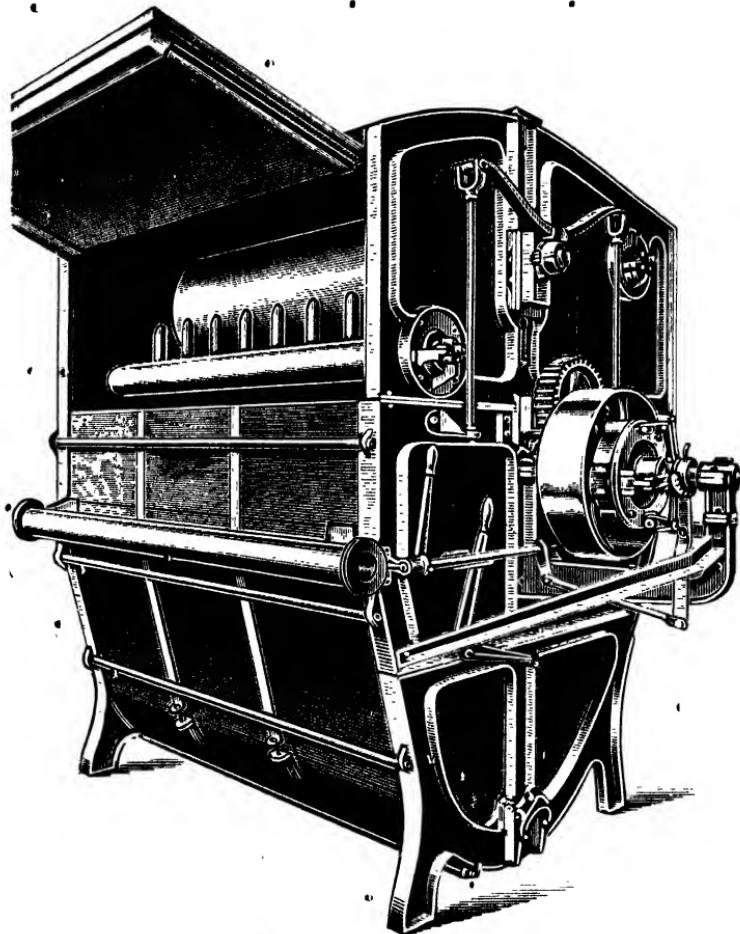


FIG. 41. Cloth-washing machine.

or less open, round which the pieces are guided—the ends of the pieces being stitched together. Pipes carrying water are so arranged that jets of clean water impinge on, and

thoroughly wash the cloth as it passes through—the construction of the guide rollers facilitating the efficient washing of the goods.

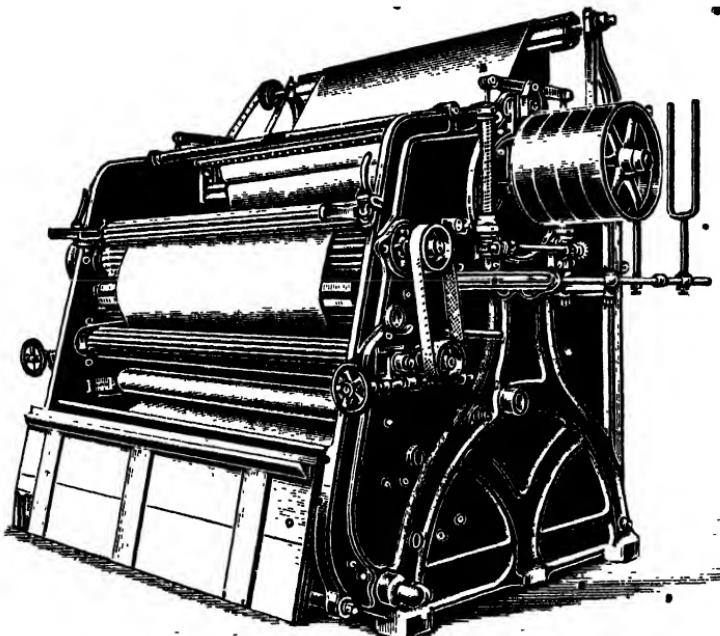


FIG. 42.—Cloth-washing machine.

**Soaping.**—Sometimes yarns or cloths have to be passed through a soap bath after being dyed in order to brighten up the colours or develop them in some way. In the case of yarns this can be done on the reel washing machine such as is shown in Fig. 39. In the case of piece goods, a continuous machine, in which the washing, soaping, etc., can be carried on simultaneously, is often employed. Such a machine is shown in Fig. 43. It consists of a number of compartments fitted with guide rollers so that the cloth passes up and down several times through the liquors in the compartments. Between one compartment and another is placed a pair of squeezing rollers. The cloth is threaded

in a continuous manner, well shown in the drawing, through the machine. In one compartment it is treated with water, in another soap liquor, in another water, and so on ; and these machines may be made with two, three or more compartments as may be necessary for the particular work in hand. As seen in the drawing, the cloth passes in at one end and out at the other finished. It is usually arranged that a continuous current of the various liquors used flows through the various compartments, thus ensuring the most perfect treatment of the cloths.

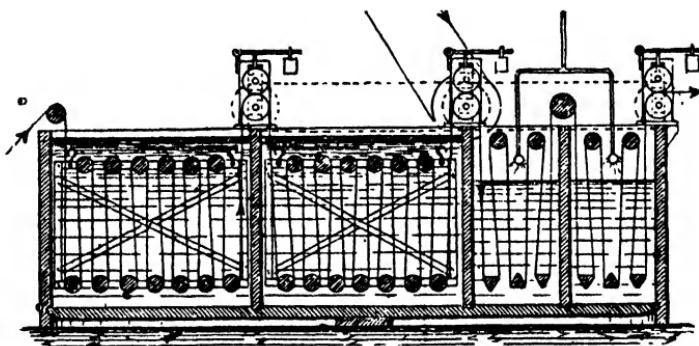


FIG. 43.—Washing and soaping vats.

**Steaming.**—Sometimes it becomes necessary to subject dyed goods to a process of steaming, as, for instance, with steam aniline blacks, khaki shades, alizarine reds, etc., for the purpose of more fully developing and fixing the dye upon the fibre. In the case of yarns, this operation is carried out in the steaming cottage, one form of which is shown in Fig. 44. It consists of a horizontal cylindrical iron vessel like a steam boiler, one end is entirely closed, while the other is made to open and be closed tightly and hermetically. The cottage is fitted with the necessary steam inlet and outlet pipes, drain pipes for condensed water, pressure gauges. The yarn to be steamed is hung on rods placed on

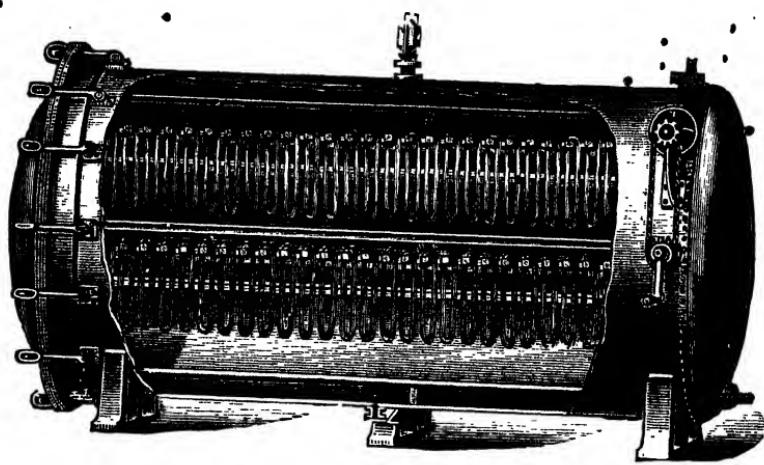


FIG. 44. - Steaming cottage.

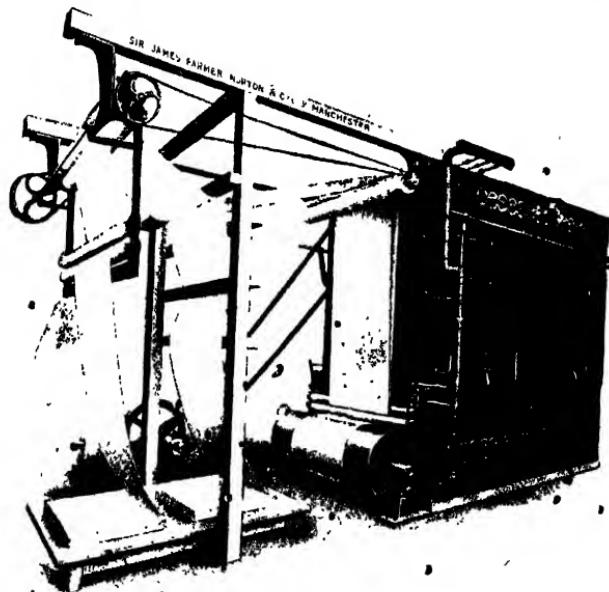


FIG. 45. - Steaming and ageing chamber. (Sir James Farmer Norton &amp; Co., Ltd.)

a skeleton frame wagon on wheels which can be run in and out of the steaming cottage as is required. The drawing shows well the various important parts of the machine. In the case of piece goods these also can be hung from rods in folds on such a wagon, but it is much more customary to employ a continuous steaming chamber, very similar to the ageing and oxidising machine shown in Fig. 45, and also used in the dyeing of aniline black.

**Drying.**—Following on the washing comes the final opération of the dyeing process, that of drying the dyed and washed goods. Textile fabrics of all kinds, after they have passed through dye-baths, washing machines, etc., contain a large amount of water, often exceeding in weight that of the fibre itself, and to take the goods direct from the preceding operations to the drying plant means that a considerable amount of fuel must be expended to drive off this large amount of water. It is therefore very desirable that the goods be freed from as much of this water as possible before they are sent into any drying chambers, and this may be done in three ways, by wringing, squeezing and hydro-extracting. The first two methods have already been described and need not again be alluded to ; the last needs some account.

*Hydro-extractors.*—Hydro-extractors are a most efficient means for extracting water out of textile fabrics. They are made in a variety of forms by several makers. Essentially they consist of a cylindrical vessel or basket, as it is called, with perforated sides so constructed that it can be revolved at a high speed. This vessel is enclosed in an outer cage. The goods are placed in the basket, and then this is caused to revolve at high speed, when centrifugal action comes into play, and the water contained in the goods finds its way to the outside of the basket through the perforations, and so away from the goods. Hydro-extractors

are made in a variety of sizes and forms—in some the driving gear is above, in others below the basket; in some the driving is done by belt-gearing, in others a steam engine or electric motor is directly connected with the basket. Figs. 46 and 47 show two forms which are much in use in the

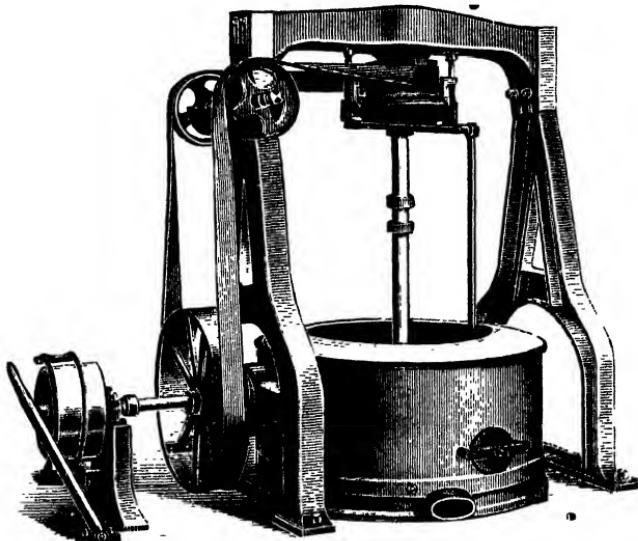


FIG. 46. Hydro-extractor, driven by belt from above.

textile industry. They are very efficient, and extract water from textile goods more completely than any other means, as will be obvious from a study of the table below. The relative efficiency of the three systems of extracting the moisture out of textile fabrics has been investigated by Grothe, who gives in his *Appretur der Gewebe*, published in 1882, the following table showing the percentage amount of water removed in fifteen minutes:—

<i>Yarns.</i>	<i>Wool.</i>	<i>Silk.</i>	<i>Cotton.</i>	<i>Linen.</i>
Wringing	44.5	45.4	45.3	50.3
Squeezing	60.0	71.4	60.0	73.6
Hydro-extracting	83.5	77	81.2	82.8

Pieces.	Wool.	Silk.	Cotton.	Linen.
Wrapping . . .	33.4	44.5	44.5	54.6
Squeezing . . .	64.0	69.7	72.2	83.0
Hydro-extracting . . .	77.8	75.5	82.3	86.0

In the practical working of hydro-extractors it is of the utmost importance that the goods be carefully and regularly laid in the basket—not too much in one part and too little

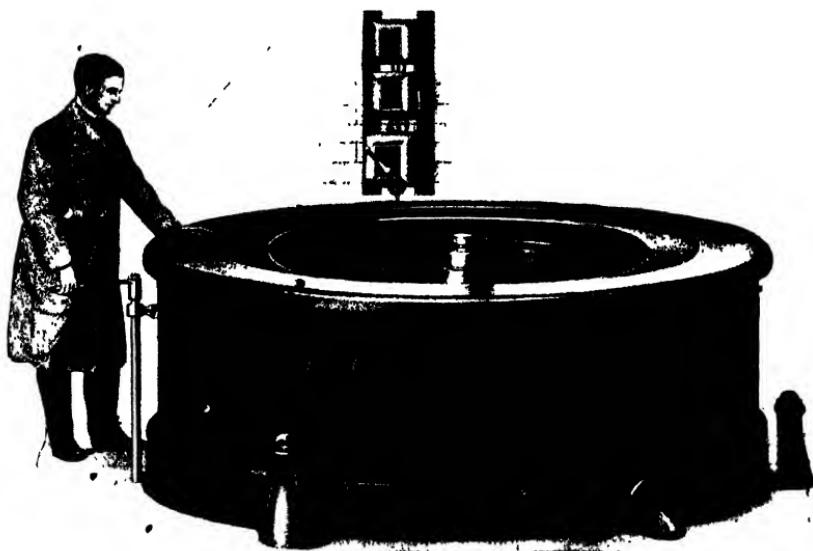


FIG. 47.—Hydro-extractor (centrifugal), under-driven.

in another. Any unevenness in this respect at the speed at which they are driven lays such a strain on the bearings as to seriously endanger the safety of the machine. *Drying Machines.*—After being wrung, squeezed or hydro-extracted, the goods are ready to be dried. In the case of yarns, this may be done in rooms heated by steam pipes placed on the floor, the hanks being lying on rods suspended from racks arranged for the purpose.

Where large quantities of yarn have to be dried, it is most economical to employ a yarn-drying machine, and one form of such is shown in Fig. 48. The appearance of the machine is that of one long room from the outside ; internally it is divided into compartments, each of which is heated up by suitably arranged steam pipes, but the degree of heating in each compartment varies—at the entrance end it is high, at the exit end lower. The yarn is fed in at one end, being hung on rods, and by suitable gearing it is carried directly through the various chambers or sections, and in its passage the heat to which it is subjected drives off the water it contains.

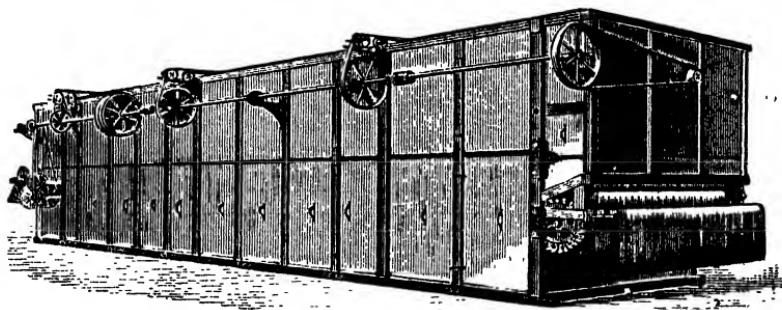


FIG. 48.—Automatic yarn-dryer.

tains. The yarn requires no attention from the time it passes in wet at the one end of the machine and comes out dry at the other end. The amount of labour required is slight, only that represented by filling the sticks with wet yarn and emptying them of the dried yarn. The machine works regularly and well. The drying is accomplished by circulating heated air through the yarns, this heating being effected by steam coils ; fresh air continually enters the chambers, while water-saturated air is as continually being taken out at the top of the chamber. One of the great secrets in all drying operations is to have a constant current of fresh hot air playing on the goods to be dried ; this absorbs the

moisture they contain, and the water-charged air thus produced must be taken away as quickly as possible. Fig. 49 shows what is called a truck yarn-dryer, which consists of a chamber heated with steam-pipes and fitted with an exhausting fan to draw out the air and water vapour which is produced. The yarns are hung on trucks which can be run in

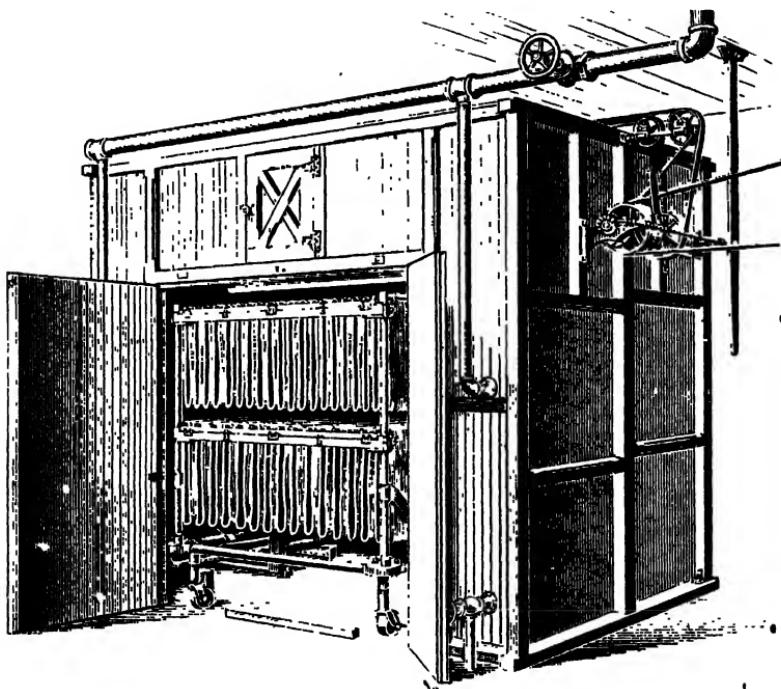


FIG. 49.—Truck yarn-dryer.

and out of the chamber for filling and emptying. *Piece Goods.*—The most convenient manner of drying piece goods is to employ the steam cylinder drying machine, such as is shown in Fig. 50. This consists of a number of hollow tin or copper cylinders which can be heated by steam passing in through the axles of the cylinders, which are made hollow on purpose. The cloth to be dried passes

round these cylinders, which revolve while the cloth passes. They work very effectually. The cylinders are arranged

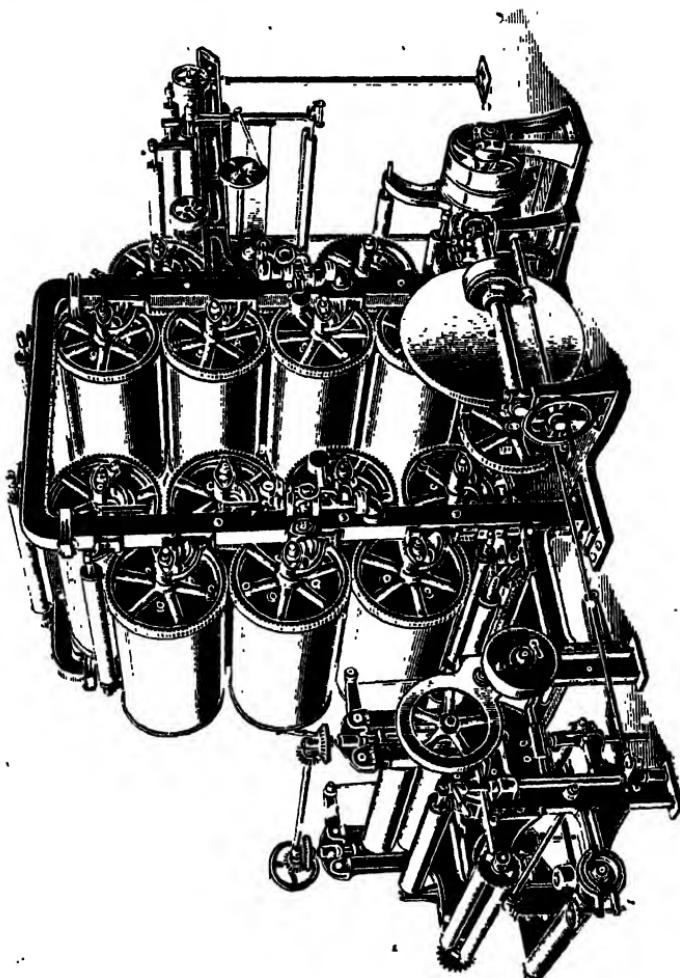


Fig. 50.—Drying cylinders.

sometimes, as in the drawing, vertically; at other times horizontally.

## CHAPTER IX

### TESTING DYED FABRICS.

ALL dyers should be familiar with the testing of dyed materials, since only by means of such knowledge can a dyer know whether the dyeings which he produces are likely to give satisfaction. Moreover, the essential methods of testing are by no means difficult or tedious.

In these days it is becoming the custom for manufacturers and cloth merchants to guarantee the fastness of the coloured fabrics which they sell, and the responsibility for these guarantees is, of course, ultimately passed on to the dyer. Hence in dyeing works, these increased responsibilities have led to the adoption of standardised methods by which the behaviour of variously dyed fabrics is tested.

In general, it is evident that dyed fabrics should be fast to light, washing, alkalis, acids, perspiration, and that their colour should not rub off. Of course, it is not often possible to dye fabrics so that they are fast to all these influences, but this is seldom necessary. Thus, while dyed carpets must be fast to light, their fastness to acids and perspiration is of little importance. On the other hand, underwear and dress materials dyed in delicate shades should be particularly fast to perspiration. On the whole, every fabric should be dyed so that it will be fast under the conditions to which it is exposed.

Methods for testing the fastness of dyed fabrics are given below :—

**Fastness to Light.**—This is an important test and may be carried out, either with artificial light or sunlight. In the latter case, the tests are, of course, dependent on weather conditions. As yet no one has succeeded in discovering exactly how sunlight causes colours to fade, but fading is undoubtedly largely due to the ultra-violet light present in it. Hence any other source of light rich in ultra-violet light is suitable for testing dyed fabrics, and several suitable lamps are sold for this purpose.

When sunlight is utilised, the dyed fabric should be exposed under cover of glass and in the presence of moisture over a period of about one month. Part of the fabric should be covered with black or otherwise opaque material, and from time to time, the exposed and covered portions may be compared.

Artificial sources of light are usually much stronger than sunlight so that the tests may be more quickly carried out, but the principle of exposure is the same.

Turkey-red dyeings will withstand several weeks exposure to strong sunlight without much fading, whereas a dyeing of Malachite green will fade at the end of one day.

**Fastness to Washing.**—For this test, a strip of the dyed fabric should be twisted together with some similar bleached cotton fabric, and then worked for about five minutes in a 0·5 per cent. solution of a neutral soap at 40° to 50° C. Afterwards, it should remain in the soap liquor for a further half hour, and then be lightly rinsed and dried.

Where it is desired to make the test more severe, the soap solution should also contain  $\frac{1}{2}$  per cent. of sodium carbonate.

In either case, the difference in shade of the *dyed material* before and after the treatment, affords a measure of the fastness to washing.

**Fastness to Alkalies.**—The dyed material should be spotted

with a 10 per cent. solution of sodium carbonate and allowed to dry, the change of shade being noted. In place of sodium carbonate, 280 ammonia may also be used.

**Fastness to Acids.**—The dyed material should be spotted with 3 per cent. hydrochloric acid. In this case the cotton cannot be dried, so that the change of shade is noted on the wet material.

**Fastness to Rubbing.**—This test is generally applied to fabrics dyed by means of insoluble dyestuffs which are produced on the fibre directly or applied by reduction and subsequent oxidation, e.g. Parlantraniline red and Indigo.

The coloured material should be vigorously rubbed on white cotton, and the extent to which the latter is soiled should be noted.

**Fastness to Perspiration.**—Human perspiration is acidic and so fabrics to be tested for their fastness to perspiration are usually tested with acetic acid. In the test, the fabric should be spotted with 50 per cent. acetic acid and the colour change noted at the end of one hour.

**Fastness to Hot-ironing.**—Many coloured fabrics change in shade when ironed, and these changes may be temporary or permanent. Hence in testing, the fabric, after being ironed in the usual manner, should be allowed to cool during half an hour and the resulting shade then noted.

**Fastness to Bleaching.**—The material should be immersed for two hours in a solution of sodium hypochlorite containing .02 grams of active chlorine per litre at the ordinary temperature. It should then be well washed, slightly acidified, thoroughly washed and dried. This, of course, is a severe test, and not many dyestuffs, excluding the vat colours, will withstand it.

## CHAPTER X.

### EXPERIMENTAL DYEING AND COMPARATIVE DYE TESTING.

EVERY dyer should be able to make experiments in the mordanting and dyeing of textile fibres for the purpose of ascertaining the best methods of applying mordants or dye-stuffs, the best methods of obtaining any desired shade, and for the purpose of making comparative tests of dyes or mordanting materials with the object of determining their strength and value. This is not by any means difficult, nor does it involve the use of any expensive apparatus, so that a dyer need not hesitate to set up a small dyeing laboratory for fear of the expense which it might entail. In order to carry out the work indicated above there will be required several pieces of apparatus. First, a small chemical balance, one that will carry 100 grams in each pan is quite large enough ; and such a one, quite accurate enough for this work, can be bought for about 50s., while a cheap pair of apothecaries' scales might be used. It is advisable to procure a set of gram weights, and to get accustomed to them. In using the balance always put the substance to be weighed on the left-hand pan, and the weights on the right-hand pan. Never put chemicals of any kind direct on the pan, but weigh them in a watch glass, small porcelain basin, or glass beaker, which has first been weighed; according to the nature of the material which is being weighed. The sets of weights are always fitted into a block or box, and every time they are used they should be put back into their proper places. The experimenter will find

it convenient to provide himself with a few small porcelain basins, glass beakers, cubic centimetre measures, two or three 200 c.c. flasks with a mark on the neck, a few pipettes of various sizes, 10 c.c., 20 c.c., 25 c.c. The most important feature is the dyeing apparatus. Where only a single dye test is to be made, a small copper or enamelled iron saucepan, such as can be bought at any ironmonger's, may be used; this may conveniently be heated by gas. It is, however, advisable to have means whereby several dyeing experiments can be made at one time and under precisely the same conditions, and this cannot be done by using the simple means noted above. To be able to

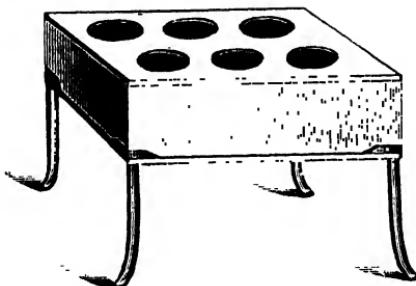


FIG. 51. Experimental dye-bath.

make perfectly comparative dyeing experiments it is best to use porcelain dye-pots—these may be bought from most dealers in chemical apparatus—and to heat them in a water-bath arrangement. The simplest arrangement is shown in Fig. 51; it consists of a copper bath measuring 15 inches long by 10½ inches broad and 6½ inches deep—this is covered by a lid in which are six apertures to take the porcelain dye-pots. The bath is heated by two round gas boiling burners of the type already referred to. The copper bath is filled with water, which, on being heated to the boil by the gas burners, heats up the dye-liquids in the dye-pots. The temperature in the dye-pots under such conditions can

never reach the boiling-point; where it is desirable, as in some cases of wool mordanting and dyeing, that it should boil, there should be added to the water in the copper bath a quantity of calcium chloride, which forms a solution that has a much higher boiling-point than that of water, and so the dye liquors in the dye-pots may be heated up to the boil. An objection might be raised that with such an apparatus the temperature in every part of the bath may not be uniform, and so the temperature of the dye-liquors in the pots may vary also, and differences of temperature often have a considerable influence on the shade of the colour which is being dyed. This is a minor objection, which is more academic in its origin than of practical importance. The dyeing laboratories of technical schools and colleges are generally provided with a more elaborate set of dyeing appliances. These, in the latest constructed, consist of a copper bath supported on a hollow pair of trunnions, that the bath can be turned over if needed. Into the bath are firmly fixed three earthenware or porcelain dye-pots; steam for heating can be sent through the trunnions. After the dyeing tests have been made the apparatus can be turned over, and the contents of the dye-pots emptied into a sink which is provided for the purpose.

Many other pieces of apparatus have been devised and made for the purpose of carrying on dyeing experiments on the small scale, but it will not be necessary to describe these in detail. After all no more efficient apparatus can be desired than that described above. Dyeing experiments can be made with either yarns or pieces of cloth—swatches, as they are commonly called; a very convenient size is a small skein of yarn or a piece of cloth having a weight of 5 grams. These test skeins or pieces ought to be well washed in hot water before use, so that they are clean and free from any size or grease. A little soda or soap will

facilitate the cleansing process. In carrying out a dyeing test the dye-pot should be filled with the water required, using as little as can be consistent with the dye swatch being handled comfortably therein, then there is added the required mordants, chemicals, dyes, etc., according to the character of the work which is being done. Of such chemicals as soda, caustic soda, sodium sulphate (Glauber's salt), tartar, bichromate of potash, it will be found convenient to prepare stock solutions of known strength, say 50 grams per litre, and then by means of a pipette any required quantity can be conveniently added. The same plan might be followed in the case of dyes which are constantly in use, in this case, 5 grams per litre will be found strong enough. Supposing it is desired to make a test of a sample of direct red, using the following proportions : 2 per cent. dyestuff, 3 per cent. soda, 15 per cent. Glauber's salt, and the weight of the swatch which is being used is 5 grams. The following calculations are to be made to give the quantities of the ingredients required.

For the dyestuff :—

5 (weight of swatch) multiplied by 2 (per cent. of dye) and divided by 100 equals—

$$\frac{5 \times 2}{100} = 0.1 \text{ gram dye.}$$

For the soda we have similarly :—

$$\frac{5 \times 3}{100} = 0.15 \text{ gram soda.}$$

For the Glauber's salt :—

$$\frac{5 \times 15}{100} = 0.75 \text{ gram Glauber's salt.}$$

These quantities may be weighed out and added to the dye-bath, or if solutions are kept, a calculation can be made

as to the number of cubic centimetres which contain the above quantities, and these measured out and added to the dye-bath.

When all is ready, the bath is heated up, the swatch entered, and the work of the test entered upon.

Students are recommended to make experiments on such points as :—

1. The shades obtained by using various proportions of dyestuffs.
2. The influence of various assistants—common salt, soda, Glauber's salt, borax, phosphate of soda—in the bath.
3. The influence of varying proportions of mordants on the shade of dyeing.
4. The value of various assistants, tartar, oxalic acid, lactic acid, sulphuric acid, on the fixation of mordants.
5. The relative value of different tannin matters, etc.

Each dyer should make himself a pattern book into which he should enter his tests, with full particulars as to how they have been produced at the side.

It is important that a dyer should be able to make comparative dye tests to ascertain the relative strength of any two or more samples of dyes which may be sent to him. This is not difficult, but requires considerable care in carrying out the various operations involved.

Of each of the samples of dyes 0.5 gram should be weighed out and dissolved in 100 c.c. of water, care being taken that every portion of the dye is dissolved before any of the solution is used in making up the dye-vats. Care should also be taken that the skeins of yarn or swatches of cloth are exactly equal in weight; that the same volume of water is placed in each of the dye-pots; that the same amount of sulphate of soda or other dye assistants are added; that the quantities of dyestuffs and solutions used are equal; in fact, that in all respects the conditions of dyeing are exactly the same,

such, in fact, being the vital conditions in making comparative dye tests of the actual dyeing strength of several samples of dyes.

After the swatches have been dyed they are rinsed and then dried, when the depth of shade dyed on them may be compared one with another. To prevent any mistakes, it is well to mark the swatches with one, two, three or more cuts as may be required.

It is easier to ascertain if two dyes are different in strength of colour than to ascertain the relative difference between them. There are two plans available for this purpose—one is a dyeing test, the other is a colorimetric test made with the solutions of the dyes.

**Dyeing Test.**—This method of ascertaining the relative value of two dyes as regards strength of colour is carried out as follows. A preliminary test will show which is stronger than the other. Then there is prepared a series of dye-vats—one contains a swatch with the deepest of the two dyes, which is taken as the standard; the others, swatches with the other dye, but containing 2, 5 and 10 per cent. more dyestuff, and all these swatches are dyed together, and after drying a comparison can be made between them and the standard swatch and a judgment formed as to the relative strength of the two dyes. A little experience will soon enable the dyer to form a correct judgment of the difference in strength between two samples of dyestuff.

**Colorimetric Test.**—This is based on the principle that the colour of a solution of dyestuff will be proportionate to its strength. Two white glass tubes equal in diameter are taken. Solutions of the dyestuff, 0.5 gram in 100 c.c. of water, are prepared, care being taken that the solution is complete. Of one of these solutions 5 c.c. is taken and placed in one of the glass tubes, and 5 c.c. of the other solution is placed in the other glass tube. Of water 25 c.c.

is now added to each tube, and then the colour of the diluted liquids is compared by looking through them in a good light. That sample which gives the deeper solution is the stronger in colouring power. By diluting the stronger solution with water until it is of the same depth of colour as the weaker, it may be assumed that the depth of the columns of liquid in the two tubes is in proportion to the relative strength of the two samples. Thus, if in one tube there are 30 c. of liquid and in the other 25 c., then the relative strength is as 30 to 25; and if the first is taken as the standard at 100, a proportion sum gives

$$30 : 25 :: 100 : 83\cdot3,$$

that is, the weaker sample has only 83·3 per cent. of the strength of the stronger sample.

The colorimetric method, though rapid, is not considered so accurate as the actual dyeing test. It should therefore be considered as an aid rather than a substitute for the latter.

THE END.



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